the Acid Deposition Research Program

BIOPHYSICAL RESEARCH

POLLUTANT EXPOSURE AND RESPONSE RELATIONSHIPS: A LITERATURE REVIEW. GEOLOGICAL AND HYDROGEOLOGICAL ASPECTS

by:

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Instrumentation Limited
Calgary, Alberta, Canada

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EXECUTIVE SUMMARY

This report forms part of the biophysical research component of the Acid Deposition Research Program (ADRP). The focus of the research is on questions of short- and long-term, observed or predicted effects of acid-forming substances on Alberta ecosystems, and their significance.

Prior to undertaking site specific research, it is essential that the state of our knowledge be determined so that a scientific starting point can be established. As the effects of atmospheric pollution are governed to a large extent by the characteristics of the receptors, it is paramount that the study identify and describe the geographic locations of receptors sensitive to acidification in Alberta.

This literature review, as one in a series, specifically addresses the geology and hydrology of Alberta, in the context of the ADRP.

Critical Literature Review

The review of relevant literature has involved the execution of computerized data base searches as well as manual searches of bibliographies and information cited in relevant literature. The three major data bases that were accessed were:

AQUALINE - Water Resource Centre
NTIS - National Technical Information Centre
DOE - US Department of Energy

The geographic distribution of areas addressed in the available literature on acidic deposition is relevant. The degree to which the results of other studies can be extrapolated to the Alberta setting is contingent upon there being major similarities between the areas previously studied and the physical and atmospheric setting in Alberta. It was found that most of the scientific work on receptor response to atmospheric pollution was conducted in Europe and the eastern part of the North American continent. Major differences exist.

pH - Buffering Mechanisms

It has been recognized that acidic input into the land-based portion of the hydrologic cycle can be neutralized if sufficient buffering agents are present, and if the rate of neutralization can balance the rate of acidic input. With time, consumption of buffering agents by the various neutralization processes may lead to the exhaustion of the neutralizing ability of the soil-rock-water system. In attempting to quantify acidification or potential acidification, scientists have used a wide range of chemical descriptors including: pH, alkalinity, cation exchange capacity, buffering capacity, calcite saturation index, acid neutralization capacity, and lime potential.

Last et al. (1980) described five neutralization processes that may be active in the subsurface. While this provides an indication of the complexity of the geochemical processes that may be active in the subsurface, Bache (1984) has contended that the two major processes that are active are: (1) cation exchange, and (2) acid hydrolysis reactions.

Strong evidence of groundwater acidification has been observed in a number of studies in the Scandinavian countries. Evidence of groundwater acidification includes declining pH values and declining alkalinity as reflected in bicarbonate values, coupled with increases in calcium and sulphate. Shallow aquifers with a low buffering capacity were most sensitive to acidification. In some localities, up to 50% of the domestic water wells had a pH below 5.5. Several municipal water supplies in deeper aquifers are also showing signs of acidification.

In Canada, analysis of water samples from wells in the Sudbury, Muskoka, and Haliburton areas in Ontario have not shown the same evidence of acidification as seen in Sweden. Only a small percentage of the water wells sampled showed depressed pH values. The author conceded, however, that due to the heavy atmospheric loading, acidification of the groundwater will occur given sufficient time.

Major Cations and Anions

The chemical constituents that are involved in the neutralization process are dependent upon the chemistry of the rock water. The major cations and anions may include:

calcium
magnesium
sodium
potassium
carbonate/bicarbonate
sulphate
chloride
nitrate

Evidence is available to suggest that the following chemical changes may be observed upon acidification:

1. Calcium concentrations will increase;
2. Sulphates will be mobilized and concentrations in groundwater may be observed if the adsorption capacity of the rock material is exceeded;
3. Carbonate/bicarbonate will decrease;
4. Chloride may become mobile and move into the water table, and no major attenuation mechanisms are apparent;
5. Nitrate levels may increase with a net beneficial effect on nitrogen-deficient soil. Once the nitrogen of the subsurface material is exceeded, nitrate will move to the water table. Once at the water table, no major attenuation mechanisms have been recognized.

Aluminum

Aluminum is one of the most abundant elements in rock materials. Due to its ubiquitous nature, aluminum is a participant in most geochemical reactions. The presence of dissolved aluminum in water is of particular concern to the scientific community because of the toxic effects of aluminum on fish. Elevated aluminum levels have been detected in both surface and groundwater in Sweden at locations where atmospheric loading has been heavy and acidification has been documented (Johansson and Hultberg 1977; Hultberg and Johansson 1978).

In laboratory leaching tests, Sparks and Curtis (1983) demonstrated that aluminum leaching increases dramatically when the pH of the leachate declines from 4.8 to 3.4. Field evidence of increased aluminum leaching with increased acidity is provided in the Laurel Hills studies conducted in southern Pennsylvania (Sharpe et al. 1984).

Metals

When pH values in the subsurface are depressed, metals become increasingly mobile. In the range of pH 3.5 to 4.0 several metals become dramatically more mobile. These elements include zinc, lead, copper, and manganese. Other metals of concern include arsenic, chromium, cadmium, nickel, mercury, iron, and selenium. It should be noted, however, that the processes of adsorption and precipitation may reduce the mobility of metals as they move from low to high pH environments.

Information currently available in the literature on the chemistry of heavy metals in natural waters and soils makes it clear that metal solubility in natural aqueous systems can be influenced by:

1. organic materials;
2. clay minerals;
3. metal hydroxides,
4. pH; and
5. divalent ions.

Groundwater Hydrology

The land based portion of the hydrologic cycle is relatively well understood and although complex, it is subject to quantification. Groundwater hydrology is a measure of physical parameters essentially unaffected by chemical processes. Although groundwater hydrology plays a major role in influencing groundwater chemistry, groundwater hydrology is largely unaffected by geochemical processes. One can be reasonably certain that basin hydrology will be unaffected by geochemical processes that may be stimulated by acidic deposition. A researcher can be confident, therefore, that the hydrology of a basin before acidic deposition is the same as the hydrology of the basin after acidic deposition occurs.

Early studies of the effects of acidic deposition tended to ignore the groundwater component of the hydrologic regime. Scientists who concentrate on the soils portion of the subsurface tend to think of groundwater as a sink for soil leachate. More recent studies have determined that groundwater constitutes almost all of base flow and a high percentage of peak flow from basin runoff. Therefore, in order to understand the

chemistry of surface water, it is essential that groundwater hydrology and groundwater chemistry also be taken into account. The ILWAS study, which is the most detailed examination of receptor response to acidic deposition, has concluded that the routing of water through a watershed is the major determinant of lake water alkalinity and vulnerability to acidification by atmospheric deposition.

Sensitivity Analysis

Early attempts to assess sensitivity of geographic areas to acidic deposition focussed on the ability of soil and rock materials to neutralize acid (Shilts 1980, cited by Saskatchewan Research Council 1981; Glass et al. 1982). A major weakness of these sensitivity evaluations is that they address only one portion of the ecological setting. It has subsequently been recognized that sensitivity of a geographic setting can only be assessed within the context of a multi-disciplinary examination of the entire ecosystem.

Modelling

The development of hydrological and geochemical models is relatively well advanced. Presently, any number of computer models exist for simulating a wide variety of groundwater scenarios in both the saturated and unsaturated zone. In the past ten years, groundwater hydrology models have been coupled with mass transport models to allow groundwater contamination problems to be simulated. Geochemical models which include PHREEQE, GEOCHEM, AND GEOCHEM II allow the simulation of complex geochemical scenarios. The ILWAS study has developed a model that has successfully simulated a variety of geochemical and hydrologic conditions of interest to researchers in the area of acidic deposition.

Human Impact

Evidence has been presented that identifies issues regarding the potential human effects from acidification of groundwater. The three major areas of concern are: (1) the acidification of groundwater leading to alteration in the distribution of major cations and anions in domestic and municipal groundwater supplies with an ensuing impact on the potability or aesthetics of the water supply; (2) leaching of toxic metals from watersheds and from water storage and distribution systems; and (3) the contamination of edible fish by toxic metals. Metals considered to be of concern include: lead, mercury, aluminum, copper, zinc, cadmium, manganese, chromium, iron, nickel, and selenium.

Resource Inventory of Alberta - Bedrock Geology

As part of this study the bedrock geology, surficial geology, and hydrogeology resources of Alberta have been inventoried using existing available information. The bedrock geology of the province has been shown in map form by Green (1972). This mapping was used as a basis for the 1:1,000,000 scale bedrock geology (Plate 1) in this report.

Basically, the bedrock geology can be simplified into the three physiographic regions: (1) the Canadian Shield which consists of Precambrian age igneous rocks; (2) the Interior Plains which are comprised of flat lying sediments of Paleozoic to Tertiary age; and (3) the Rocky Mountain Cordillera which is comprised of folded and faulted sediments of Precambrian to Tertiary age.

Cretaceous and Tertiary sediments are the most common, being the uppermost bedrock strata over all of the Interior Plains region with the exception of that along the Canadian Shield.

Sandstones of this areas are typically non-marine to deltaic, fine-grained, and often poorly indurated. Shales are generally non-marine in the southern half of the province and marine in the north. Montmorillonite clay predominates in non-marine shales and illite predominates in marine shales.

Metals in Alberta bedrock vary regionally with the various formations. Iron, zinc, copper, and boron are dominant in the northwest, associated with the marine shales of that region. Manganese is mainly found in southern and central Alberta, associated with ironstone nodules in non-marine bedrock units.

Resource Inventory of Alberta - Surficial Geology

The 1:1,000,000 scale surficial geology map of Alberta (Plate 2) has been assembled using mapping by the Geology Branch of the Research Council of Alberta, the Geological Survey of Canada, the Exploratory and Reconnaissance Soil Survey of Alberta Research Council, and Special Geomorphic Landform Maps (Environment Canada and Alberta Energy and Natural Resources, Parks Canada Biophysical Inventory, and Atlas of Alberta 1969).

The majority of the province (70%) is covered by till. Glaciolacustrine deposits cover significant portions of the northern half of the province, whereas glaciofluvial and eolian materials are most common in the eastern and northeastern portions of Alberta. Alluvium is distributed throughout the province along the streams and rivers, the valley walls of which are often covered with colluvium. Colluvium is also found on mountain slopes and on the unglaciated areas of the province. Organics constitute the final genetic type, and infill poorly-drained, depressional areas and are particularly prevalent in the north.

Chemical and physical composition of surficial deposits is generally a function of the source. For tills, the underlying bedrock is the main source of material. In the south, tills tend to be clay loam in texture and montmorillonite-rich. In the north, where marine shales are common, tills are usually heavy in illite clay. The tills near the mountains and Shield areas are usually coarser and have higher carbonate contents. As well, metal contents are similar to those of the underlying bedrock, with their distribution being similar to that outlined earlier for bedrock.

Characteristics of other genetic types of surficial deposits have not been studied in much detail. Glacial lake sediments are like tills in their clay mineralogy and carbonate content.

Glaciofluvial, alluvial, and eolian materials differ from locality to locality and even within a given deposit. Both glaciofluvial and alluvial deposits have their source in part from the west and in part from local derivation. As a result, chemical and physical characteristics are dependent on distance from mountains and on the local geology.

Resource Inventory of Alberta - Hydrogeology

Groundwater is used extensively in the province for domestic, municipal, industrial, and agricultural purposes. There are currently about 2330 groundwater licences in Alberta (a licence required for any continuous pumping rate that exceeds 23 m^3/d) with industry, municipal, agricultural, and miscellaneous uses accounting for 33%, 29%, 28% and 9%, respectively. In addition, there are an estimated 250,000 unlicenced water wells used for rural domestic water supply.

The main licenced groundwater demands in Alberta are for municipal and industrial use in the areas of the North and South Saskatchewan River basins. Groundwater demands in the Peace, Athabasca, and Red Deer River basins are about half that (40,000-61,700 $dams^3/y$) of the two major areas. Use in the northern areas has been mainly industrial (petroleum), whereas in the Red Deer basin, municipal and agricultural users predominate.

Mapping of hydrogeological resources has been completed for the province by the Alberta Research Council. The major aquifers in southern Alberta are sandstones - the Paskapoo (west central Alberta), the Milk River (southern Alberta), and Lower Belly River Formations (east central Alberta). In the northern half of the province, buried channels have the best potential for large groundwater supplies.

Groundwater chemistry varies markedly in Alberta, the result of differences in geology, topography, climate, vegetation, and soils. The Hydrogeological Maps of Alberta contain regional information on chemistry of groundwater.

Groundwater flow is a function of geology, topography, and gravity, with three hydrogeological regimes existing (Toth 1963): local, intermediate, and regional systems.

Conclusions and Implications

Based on our understanding of the science of hydrogeology and our understanding of acidic deposition, there is a reasonable scientific basis for concern about the impact of atmospheric pollution on our groundwater resources. There is strong scientific evidence, particularly from Sweden, which relates acidic deposition to changes in groundwater chemistry. In Canada, there is no conclusive evidence of changes in groundwater chemistry due to acidic deposition. However, it has been concluded by the studies on groundwater conducted in Ontario that, given sufficient atmospheric loading over a long enough period, changes in groundwater chemistry would occur. Groundwater resources in the province of Alberta are utilized extensively for domestic, agricultural, municipal, and industrial purposes. Changes in groundwater chemistry in Alberta could therefore have a dramatic effect on the well-being of persons relying on groundwater for their water supply.

Acidification of groundwater may be characterized by the changes in the chemistry of groundwater. These changes may include, but are not necessarily restricted to:

1. a reduction in pH;
2. a reduction in alkalinity as reflected by bicarbonate concentrations;
3. an increase in major cations (Ca, Mg, Na, K);

4. in increase in the concentrations of sulphate;
5. an increase in chloride concentrations;
6. an increase in nitrate concentrations;
7. an increase in the silica concentrations;
8. an increase in the dissolved aluminum; and
9. an increase in mobility of dissolved metals including lead, mercury, copper, zinc, cadmium, manganese, chromium, iron, nickel, and selenium.

The geochemical processes that could produce these changes are complex. Simple chemical models such as those based on solubility of single elements do not adequately describe the geochemical processes present in the ecosystem. The extrapolation of the results of studies undertaken in Sweden and eastern United States is tenuous due to significant differences in the physical setting of these areas compared to Alberta.

In Alberta, groundwaters are characterized by relatively high pH (6.5 - 8.0) values and high acid neutralization capacity. Although groundwater chemistry data in the northern part of the province are limited, Schwartz (1979, 1980) suggested that even in muskeg areas, groundwater is characterized by pH values in the 6.5 - 8.0 range.

Much of Alberta is covered with relatively thick deposits of glacial till that have a high acid neutralization capacity. It is doubtful if acidification of groundwater in these deposits would occur in the short term given the present level of atmospheric loading. It may, however, be possible to see the residues or byproducts of the acid neutralization process in selected aquifers.

Krouse et al. (1984) have found evidence in the west Whitecourt area which suggests that the products of acid neutralization reactions have reached the water table.

Aquifers in Alberta which are most likely to show some documentable response to acidic deposition would be characterized by:

1. low buffering capacity;
2. rapid recharge;
3. shallow, short flow regime; and
4. high permeability.

Geological settings that are likely to reflect the above-mentioned hydrogeological characteristics would occur where aeolian or glaciofluvial deposits overlie dense low permeability glacial till or bedrock.

The role of hydrology in determining sensitivity of a watershed to acidic deposition has been underestimated by a number of researchers. This author concludes that the sensitivity of a specific geographic area to acidic deposition can only be accurately assessed within the context of the entire ecosystem. The role that groundwater plays in the ecosystem is a major one.

Research Needs

Based on the review of existing literature and the regional review of the hydrogeology of Alberta, it has been concluded that there is a limited risk of serious, widespread impacts on groundwater chemistry by acidic deposition. Locally, however, certain aquifers may be more sensitive to acidic deposition than others. Unfortunately, there are no data presently available in Alberta to support or refute this hypothesis.

It is felt, therefore, that in order to meet the objectives of the Acid Deposition Research Program, the hypothesis must be tested. To test the hypothesis, it is recommended that a study be undertaken to:

a. document the response of the most sensitive aquifers in Alberta to acid loading;
b. document the response of moderate or low sensitivity aquifers in Alberta to acid loading;
c. determine background levels of specific metals and ions in Alberta groundwaters and the temporal variations in these constituents; and
d. characterize the groundwater chemistry in muskegs in northern Alberta so that sensitivity of these regions can be assessed.

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1. INTRODUCTION

There are few comprehensive studies relating air pollution to ecosystem effects, but there are many studies which address specific components within the ecosystem. A serious deficiency is the unsatisfactory numerical explanation of the actual relationship between exposure and observed effects. In many cases, multi-component interfaces (e.g., vegetation/soil) are poorly described or the actual cause and effect relationship is tenuous. Therefore, an extensive and critical analysis of the state of our knowledge of the effects of acid forming substances on agronomic and forest ecosystems must be developed. The nature of short- or long-term effects of atmospheric pollution is governed, to a large extent, by the characteristics of the receptors. It is paramount, therefore, that effects studies identify and describe the geographic locations of receptors sensitive to acidification.

The purpose of this report is to provide an inventory and literature review of the geological and hydrogeological aspects relevant to the discussion of acidic deposition effects in Alberta.

2. CRITICAL LITERATURE REVIEW

Prior to undertaking an extensive research effort on the effects of atmospheric pollutants on the ecosystem, one must define a scientific starting point. In this review, the starting point will consist of a description and evaluation of the state of the science with regard to the impact of atmospheric pollution on groundwater. A critical task which needs to be completed involves integration of: (a) key, known criteria of receptor (e.g., plant species and soil) sensitivity to acidic substances and acidification processes; (b) geographic distribution of receptor sites in Alberta (both agronomic and forested); and (c) geographic distribution of sources of acid forming substances. This effort must be completed in cooperation with scientists performing point source apportionment studies.

Once the synthesis of existing literature is complete and atmosphere-effects relationships have been derived from such efforts, the Alberta air quality data (gathered in this research program) and Alberta receptor types (their possible responses being derived from the literature search) must be interfaced to derive present and potential effects in Alberta.

For this report, the review of relevant literature has been executed through use of computerized information bases as well as manual searches of bibliographies and information cited in relevant literature. A comprehensive literature review of the hydrogeological implications of acidic deposition was undertaken in three phases. In the early stages of the project, a manual, preliminary literature search and evaluation of specific known projects which included a hydrogeological component was conducted. The most notable of these studies was the Integrated Lake-Watershed Acidification Study (ILWAS) (Tetra Tech Inc. 1984) undertaken in the Adirondack Mountains of the eastern United States. The information derived from this phase of the literature search was used in the provisional assessment of geological and hydrologic receptors with specific reference to the Alberta setting. The preliminary literature review allowed more specific areas of technical concern to be identified for the computerized literature search.

In the second phase of the literature review, computer searches of data bases were executed using keywords to identify a core of background literature relevant to the hydrogeological aspects of acidic deposition. The three major data bases which were accessed included:

AQUALINE - Water Resource Centre
NTIS - National Technical Information Service
DOE - US Department of Energy

The third phase of the literature search consisted of a manual search for relevant material cited in the literature thus far obtained through Phases I and II. Much of the literature obtained was available through The University of Calgary, the Kananaskis Centre Resource Room (ADRP) Library, or the Canadian Institute for Science and Technology Information at the National Research Council of Canada. Articles that could not be obtained from these sources were obtained directly from the publishing agency or the original author.

The geographic location of the previously conducted research on acidic deposition is significant. The literature search revealed that much of the early scientific work on the hydrogeological responses to acidic deposition was conducted in Europe, notably in the Scandinavian countries, and to a lesser degree, in continental Europe and Great Britain. In North America, studies have most frequently been conducted where atmospheric loading is most intense. One finds, therefore, that much of the scientific effort on the subject of acidic deposition occurs in the northeastern United States and eastern Canada.

The relevance of previous "acidification" studies and the degree to which their results can be extrapolated to the Alberta setting is, to a large extent, contingent upon there being major similarities between those geographic areas previously studied and the physical and atmospheric setting in Alberta. A prime objective of the ADRP is to develop a model to predict the impact of acidic deposition in Alberta. To meet this objective, it is of paramount scientific importance that a clear understanding be achieved of the mechanisms (both naturally occurring and anthropogenic) that contribute to the acidification of the environment.

In considering the potential impact of acidic deposition, one may begin with two very simple working hypotheses. The first states that atmospheric deposition does not interact with the terrestrial or aquatic ecosystem and that the ecosystem acts as a biologically and chemically inert pipeline that moves the materials deposited on the earth's surface from the point of deposition to an end point in the terrestrial system.

The second hypothesis considers that atmospheric deposition interacts physically, chemically, and biologically with the terrestrial and aquatic ecosystem as the materials deposited are moved from the point of deposition to some end point in the ecosystem. Under this hypothesis, the assessment of potential impact from acidic deposition requires an understanding of physical, chemical, and biological mechanisms which such deposition will be exposed to as it moves through the ecosystem.

It is intuitively obvious that the first hypothesis is invalid and that any comprehensive assessment of potential impact of acidic deposition requires an understanding of the physical, chemical, and biological processes. Not only is an understanding of individual processes required but an understanding of how each of these processes or mechanisms interacts is also necessary. When one considers the number of environmental variables that influence ecological processes, an appreciation is gained of the danger of extrapolation based on the measurement of a limited number of ecological parameters.

Before attempting to discuss the potential impact of atmospheric deposition on groundwater it is essential, then, that we be able to describe hydrogeological and hydrogeochemical processes in scientific terms. Only through this understanding will it be possible to predict how the hydrogeological regime will respond to the external stresses imposed by acidic deposition. Fortunately, the disciplines of hydrogeology and hydrogeochemistry are relatively well established with a scientific framework that describes these components of the ecosystem.

In keeping with this emphasis on a "holistic" scientific approach, a literature review of the scientific discussion of potential impact is properly prefaced by a brief, and albeit incomplete, discussion of the physical, chemical, and biological processes active in an unstressed ecosystem. The literature review will then discuss relevant

scientific efforts that consider the potential impact of anthropogenic atmospheric deposition on these processes.

2.1 GROUNDWATER HYDROLOGY

In considering the potential impacts of acidic deposition on the environment, there must be a clear understanding from the outset that our ecosystems consist of a complex assemblage of dynamic and interrelated physical, chemical, and biological processes. Ecosystems are not in a steady state and therefore some understanding of the ecosystem mechanisms is a prerequisite to assessing the potential impact of external factors such as acidic deposition.

The discipline of groundwater hydrology has been widely discussed by a number of internationally respected scientists. Perhaps the most lucid and comprehensive overview of groundwater hydrology was provided by Freeze and Cherry (1979). In this report, the work of Freeze and Cherry has been cited extensively.

The endless circulation of water between ocean, atmosphere, and land is called the hydrologic cycle. This is the essence of the hydrologic cycle, as shown in the simplified diagram of Figure 1 illustrating the cycle schematically. A generalized equation of the hydrologic cycle can be expressed as:

$$\text{Inflow} = \text{Outflow} \pm \text{Storage} \qquad [1]$$

The hydrologic cycle may be further subdivided into components as indicated in Figure 2, and each of these components can be quantified with due scientific diligence. Further, the following formula allows the volume of water that is moving in individual locations in the hydrologic cycle to be quantified:

$$P = Q + E + \Delta S_s + \Delta S_g \qquad [2]$$

where: P = precipitation
Q = runoff
E = evapotranspiration
ΔS_s = change in surface water storage
ΔS_g = change in groundwater storage

Groundwater hydrology may be defined as the science of the occurrence, distribution, and movement of water below the surface of the earth. This report focusses on the land based subsurface portion of the cycle as it might be operative in an individual watershed. Inflow to the land based portion of the hydrologic system arrives as precipitation. Outflow occurs as streamflow (or runoff) and as evapotranspiration. Precipitation is delivered to streams both on the land surface as overland flow to tributary channels, and by subsurface flow routes as interflow and baseflow following infiltration into the soil. Groundwater referred to without further specification is commonly understood to mean water occupying all the voids within a geologic stratum. This saturated zone is to be distinguished from an unsaturated or aeration zone where voids are filled with water and air. Unsaturated zones are usually found above saturated zones and extending upward

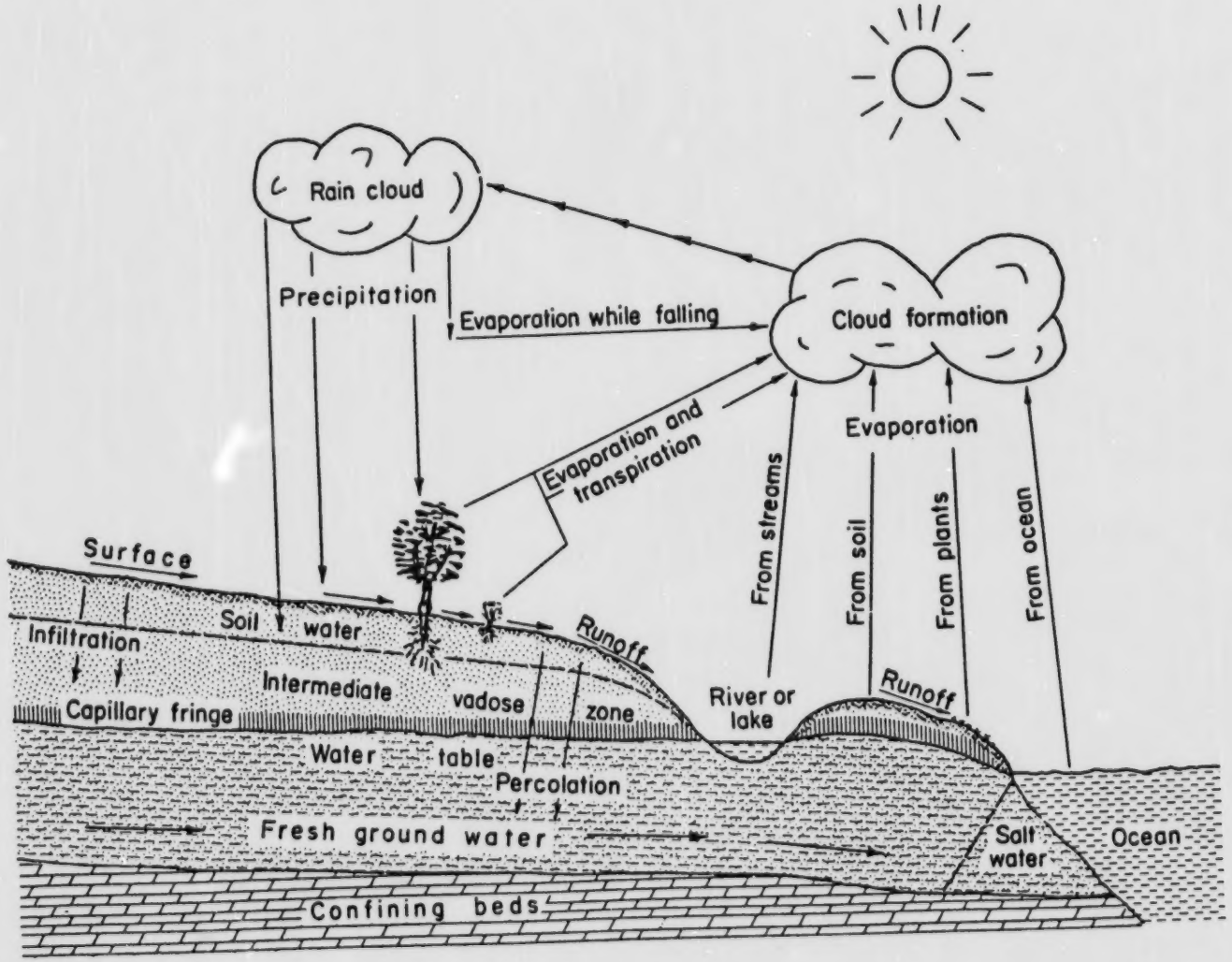

Figure 1. Schematic diagram of the hydrologic cycle. Source: Universal Oil Products Co. (1972)

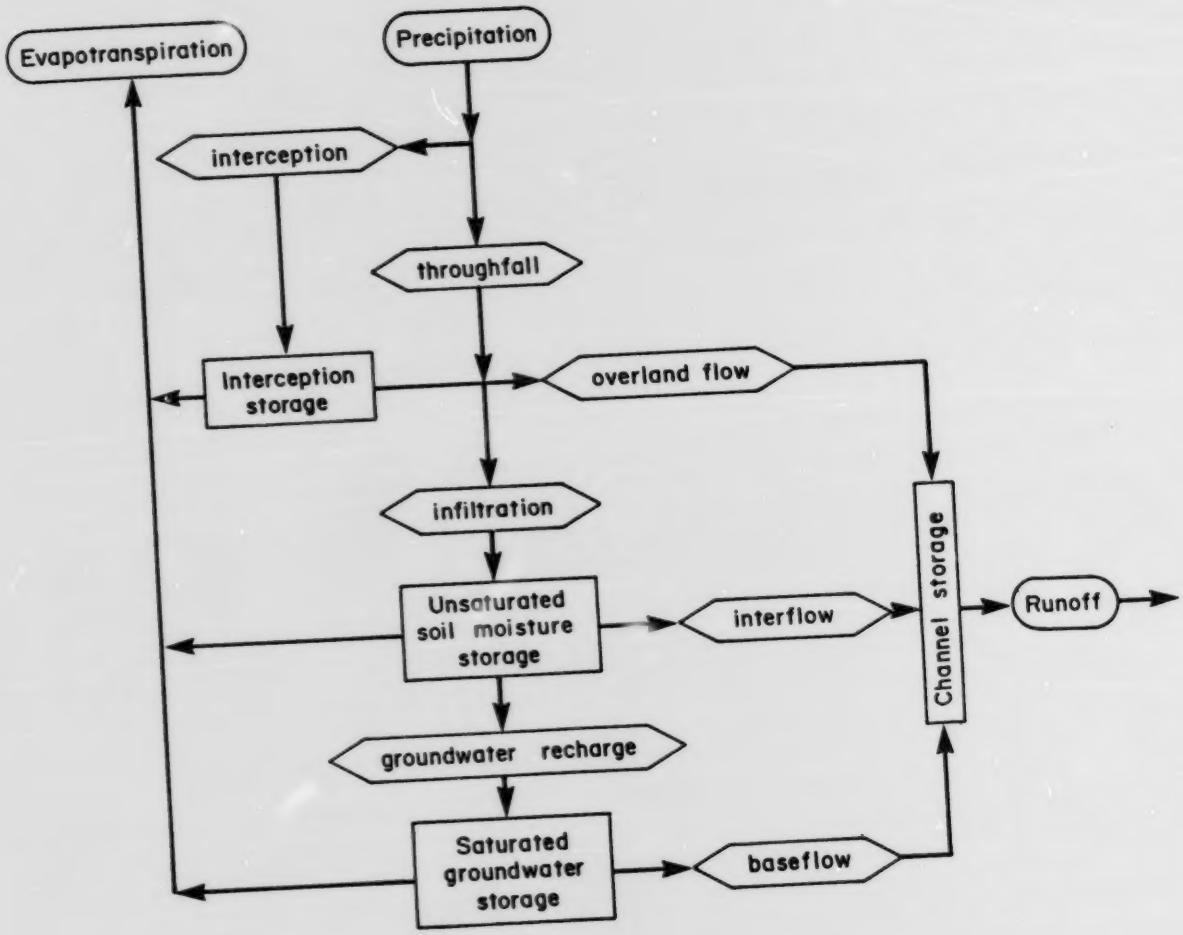

Figure 2. Systems representation of the hydrologic cycle. Source: Freeze and Cherry (1979)

to the ground surface. No rigid demarcation between the two zones is possible, for they possess an interdependent boundary and water can move from zone to zone in either direction. Water-bearing formations of the earth's crust act as conduits for transmission and as reservoirs for the storage of water. Water enters these formations from the ground surface or from bodies of surface water, and subsequently travels slowly for varying distances until it returns to the surface by action of natural flow, plants, or man.

Groundwater emerging into surface stream channels aids in sustaining streamflow when surface runoff is low or nonexistent. A basic groundwater equation which permits the quantification of groundwater flow states:

$$\Delta S_{gw} = \text{recharge} - \text{discharge} \qquad [3]$$

where ΔS_{gw} is the change in groundwater storage during the period of study. Theoretically, under natural conditions and over a long period of time which includes both wet and dry cycles, ΔS_{gw} will be zero, and inflow (recharge) will equal outflow (discharge). Recharge from natural sources includes the following:

1. deep percolation from precipitation;
2. seepage from lakes and streams;
3. underflow from another aquifer; and
4. artificial recharge.

Discharge from the groundwater reservoir occurs in the following ways:

1. seepage to streams;
2. flow from springs and seeps;
3. evaporation and transpiration; and
4. artificial discharge.

The more rigorous methods available for the evaluation of the groundwater flow regime address the aspects of recharge and discharge in varied degrees of detail; however, the basic equation [3] is common to all techniques.

As discussed above, the subsurface occurrence of groundwater may be divided into zones of saturation and aeration (Figure 3). In the zone of saturation, all interstices are filled with water under hydrostatic pressure and, hence, the porosity is a direct measure of the water contained per unit volume.

The saturated zone is bounded at the top by either a limiting surface of saturation or overlying impermeable strata, and extends down to underlying impermeable strata such as clay beds or bedrock. In the absence of overlying impermeable strata, the upper surface of the zone of saturation is the water table, or phreatic surface. This is defined as the surface of atmospheric pressure and would be revealed by the level at which water stands in a well that penetrates the aquifer. Actually, saturation extends slightly above the water table owing to capillary attraction; however, water is held there at less than atmospheric pressure. Water occurring in the zone of saturation is commonly referred to as "groundwater."

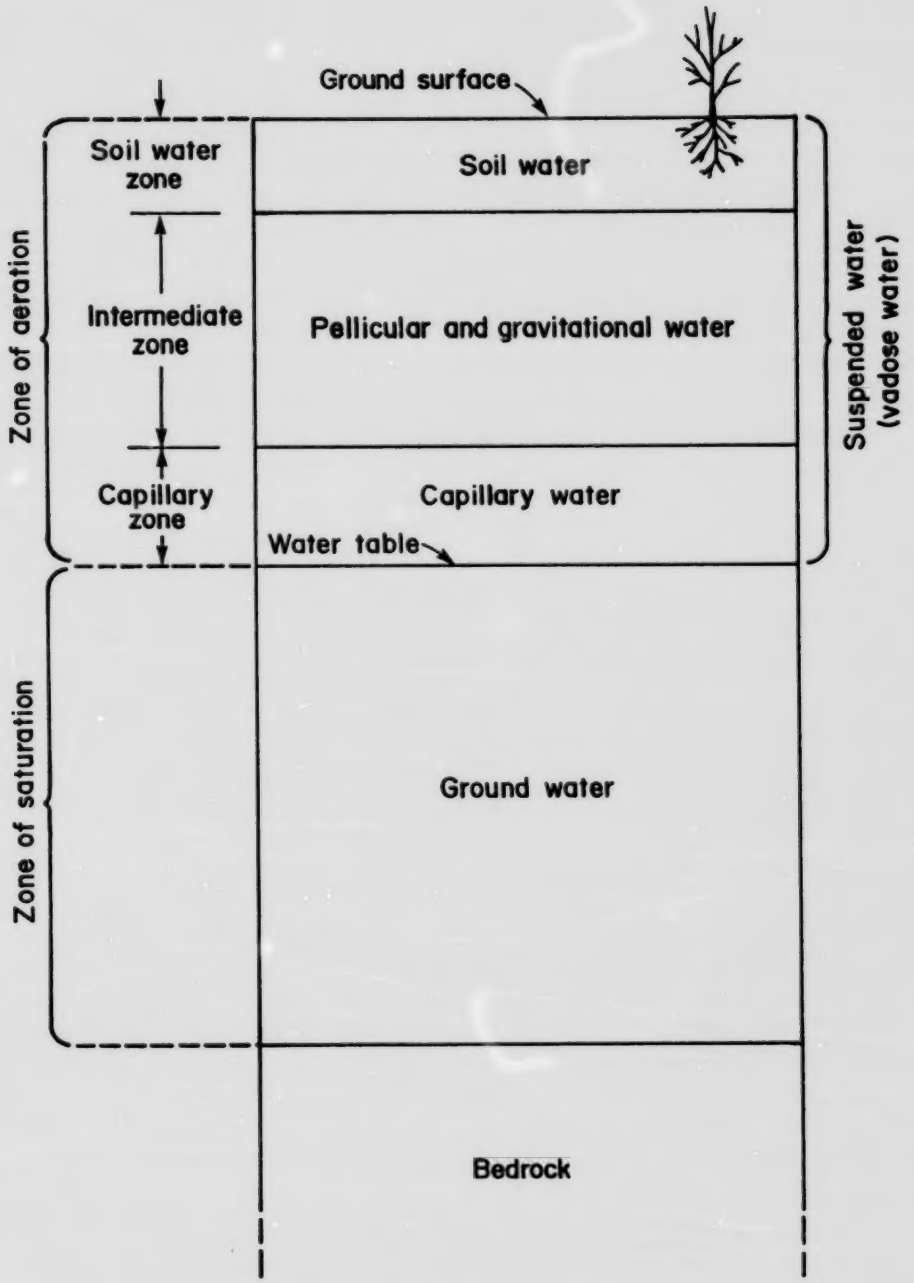

Figure 3. Schematic diagram of the zone of aeration. Source: Todd (1959)

In the zone of aereation, suspended or vadose water occurs. This general zone may be further subdivided into the soil water zone, intermediate zone, and the capillary zone (Figure 3). Water in the soil water zone exists at less than saturation except temporarily, when excess water reaches the ground surface from rainfall or irrigation. The zone extends downward from the ground surface through the major root zone. Its thickness varies with soil type and vegetation. Soil water has long been classified (Briggs 1897, cited by Todd 1959) in three categories dependent upon its concentration in the soil zone: hygroscopic, capillary, and gravitational.

Hygroscopic water adsorbed from the air forms thin films of moisture on soil particle surfaces. The adhesive forces are very large, so that this water is unavailable to plants. Capillary water exists as continuous films around the soil particles. It is held by surface tension, is moved by capillary action, and is available to plants. Gravitational water is excess soil water which drains through the soil under the influence of gravity.

The intermediate zone extends from the lower edge of the soil water zone to the upper limit of the capillary zone. This zone may vary in thickness from zero where the bounding zones merge with a high water table approaching the ground surface, to several hundred metres under deep water table conditions. Non-moving or pellicular water is held in place by hygroscopic and capillary forces. Gravitational water may also be moving downward through the intermediate zone.

The capillary zone extends from the water table up to the limit of capillary rise of water. Mavis and Tsui (1939, cited by Todd 1959) found that the maximum capillary rise in inches could be approximated by the equation:

$$H_c = \frac{2.2}{dH} \left(\frac{1 - a}{a^x} \right)^{2/3} \qquad [4]$$

Not only will the thickness of the capillary zone vary with soil or rock texture, but for a given stratum containing innumerable pores with a wide range of size, the upper limit will also form a jagged edge when studied microscopically. Macroscopically, however, there results a gradual decrease in moisture content with increasing height. This distribution of moisture above the water table is shown in Figure 4 from drainage test data by Lambe (1951, cited by Todd 1959).

Movement of water under conditions of less than saturation takes place in the zone of aeration as a result of capillary and gravitational forces. Experimental evidence indicates that unsaturated flow obeys Darcy's Law but with a different permeability than for saturated flow. In fact, the lower the degree of saturation, the lower the permeability. Physically, this is logical because with a portion of the voids occupied by air, water is impeded in its passage through porous media. Permeability approaches zero near the threshold saturation, indicating no flow. At this lower limit, water is held primarily by capillary forces and is distributed in individual concentrations in the smaller pore spaces. Laboratory experiments with sand channels by Mavis and Tsui (1939, cited by Todd 1959) demonstrated that flow parallel to the water table occurs in the capillary zone. As might be anticipated, velocities in the unsaturated zone decrease with distance above the water table. It has been shown from experimental evidence that

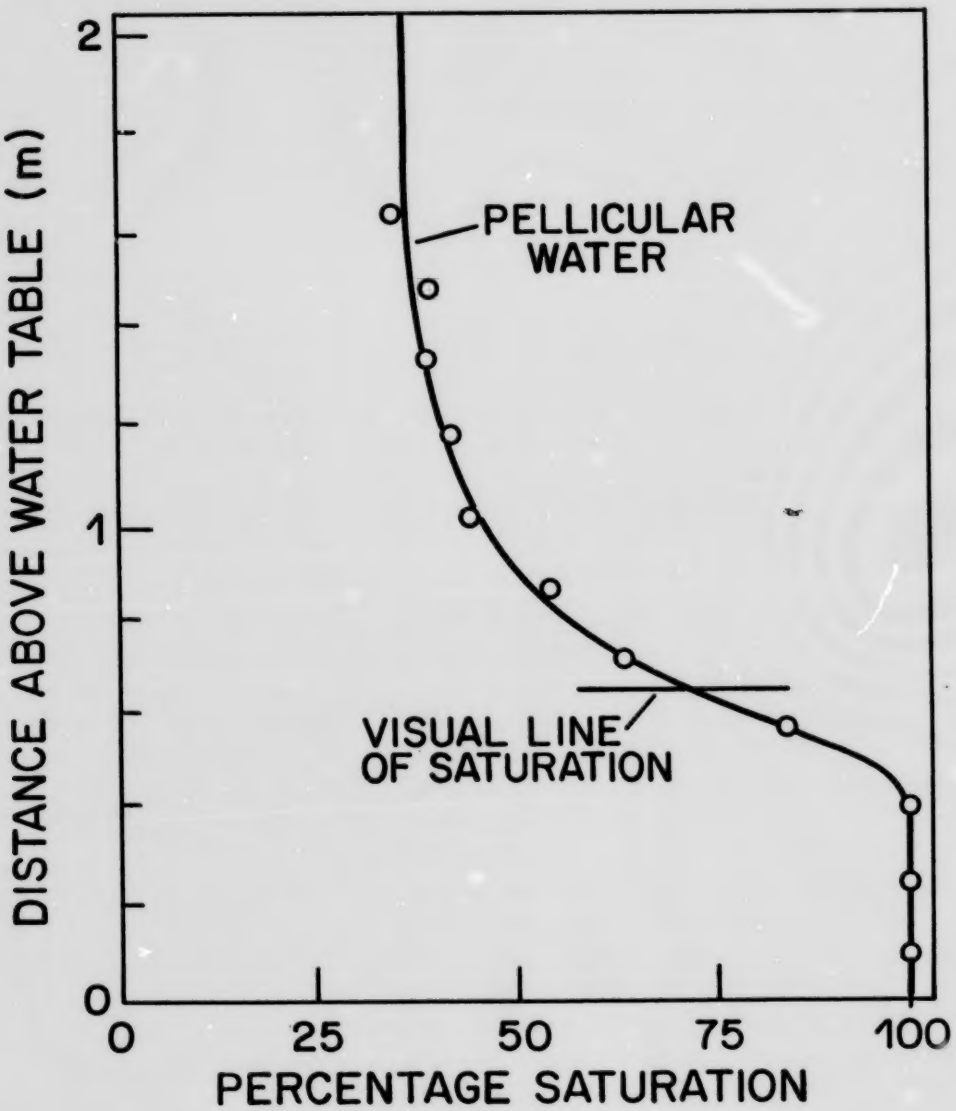

Figure 4. Distribution of moisture in a fine sand. Source: Lambe (1951), in Todd (1959)

unsaturated horizontal flow into a dry medium originating from a constant saturated source can be expressed by:

$$V = Ct^{\frac{1}{2}} \qquad [5]$$

where: V = velocity
C = a constant
t = time

For upward and downward flow, more complex expressions relating velocity to time have been derived. Laboratory studies of one-directional flow from free surface through unsaturated soil indicate three distinct moisture zones. The first is the wetting front, representing the initial capillary fringe of the advancing water. The wetting zone follows, beginning with moisture in the conducting pores and extending downward until a moisture equilibrium is reached. Finally, the transmission zone is formed and contains an essentially constant moisture content which approximates 80% of saturation.

Groundwater recharge may be defined as the entry into the saturated zone of water made available at the water table surface, together with the associated flow away from the water table within the saturated zone.

Groundwater discharge may be defined as the removal of water from the saturated zone across the water table surface, together with the associated flow toward the water table within the saturated zone.

The process of infiltration is the entry into the soil of water made available at the ground surface, together with the associated flow away from the ground surface within the unsaturated zone. Ex-filtration is the removal of water from the soil across the ground surface, together with the associated flow toward the ground surface within the unsaturated zone.

The process of infiltration has been widely studied by both hydrologists and soil physicists. In hydrology, Horton (1933, cited by Todd 1959) showed that rainfall, when it reaches the ground surface, infiltrates surface soils at a rate that decreases with time. He pointed out that for a given soil there is a limiting curve that defines the maximum possible rates of infiltration versus time. For heavy rains, the actual infiltration will follow this limiting curve which Horton called the curve of infiltration capacity of the soil. The capacity decreases with time after the onset of rainfall and ultimately reaches an approximately constant rate. The decline is caused mainly by the filling of the soil pores with water. Controlled tests carried out on various soil types by many hydrologists over the years have shown that the decline is more rapid and the final constant rate is lower for clay soils with fine pores than for open textured, sandy soils. If at any time during a rainfall event the rate of rainfall exceeds the infiltration capacity, excess water will pond on the soil surface. It is this ponded water that is available for overland flow to surface streams. Scientific contributions by Philip (1957a,b,c,d,e and 1958a,b, cited by Freeze and Cherry 1979) and Rubin et al. (1963,1964, cited by Freeze and Cherry 1979) have allowed the actual infiltration rate to be quantified.

The question of whether a given input and a given set of initial conditions and soil type will give rise to groundwater recharge is actually a question of whether this set of conditions will result in a water table rise. This rise provides the source of replenishment that allows the prevailing rate of recharge to continue. The possibility of a water table rise is greater for: (1) low intensity rainfalls of long duration rather than high intensity rainfalls of short duration; (2) shallow water tables rather than deep ones; (3) low rather than high groundwater recharge rates; (4) wet antecedent moisture conditions rather than dry conditions; and (5) soils whose characteristic curves show high conductivity, low specific moisture capacity, or moisture content over a considerable range of pressure-head values.

The mechanisms of infiltration and groundwater recharge are not always one-dimensional. In hilly areas, certain portions of a groundwater recharge area may never receive direct infiltration to the water table. Rather, recharge may be concentrated in depressions where temporary ponds develop during storms or snowmelt periods. Lissey (1968) has referred to this type of recharge as depression focussed. Under such conditions, the water table still undergoes a basin-wide rise. The rise is due to vertical infiltration beneath the points of recharge and subsequent horizontal flow toward the water table depression created between these points.

The relationship between rainfall and runoff is at the very core of hydrology. In a scientific sense, there is a need to understand the mechanisms of watershed response. In an engineering sense, there is a need for better techniques for the prediction and quantification of runoff from rainfall and infiltration.

The path by which water reaches a stream depends upon such controls as climate, geology, topography, soils, vegetation, and land use. In various parts of the world and even in various parts of the same watershed, different processes may generate streamflow, or the relative importance of the various processes may differ. Nevertheless, it has been recognized that there are essentially three processes that feed streams. As illustrated in Figure 5, these are overland flow, subsurface stormflow (or interflow), and groundwater flow. An insight into the nature of the subsurface flow regime is necessary for an understanding of the production of runoff by any of these three mechanisms.

Although the regional groundwater flow regime may sometimes contribute to runoff during storms, its primary role is in sustaining streams during low flow periods between rainfall and snowmelt events.

The classic concept of streamflow generation by overland flow originated with Horton (1933, cited by Todd 1959). The dependence of overland flow on the infiltration regime in the unsaturated surface soils of a watershed has been discussed. As originally presented, Horton's theory implied that most rainfall events exceed infiltration capacities and that overland flow is common and areally widespread. Later, researchers recognized that the greater heterogeneity in soil types at the ground surface over a watershed and the very irregular patterns of precipitation in both time and space, create a very complex hydrologic response on the land surface. This led to the development of the partial-area-contribution concept (Betson 1964, cited by Freeze and Cherry 1979; Ragan 1968, cited by Freeze and Cherry 1979), wherein it is recognized that certain portions of the watershed regularly contribute overland flow to streams, whereas others seldom or never do. The conclusion of most recent field studies is that overland flow

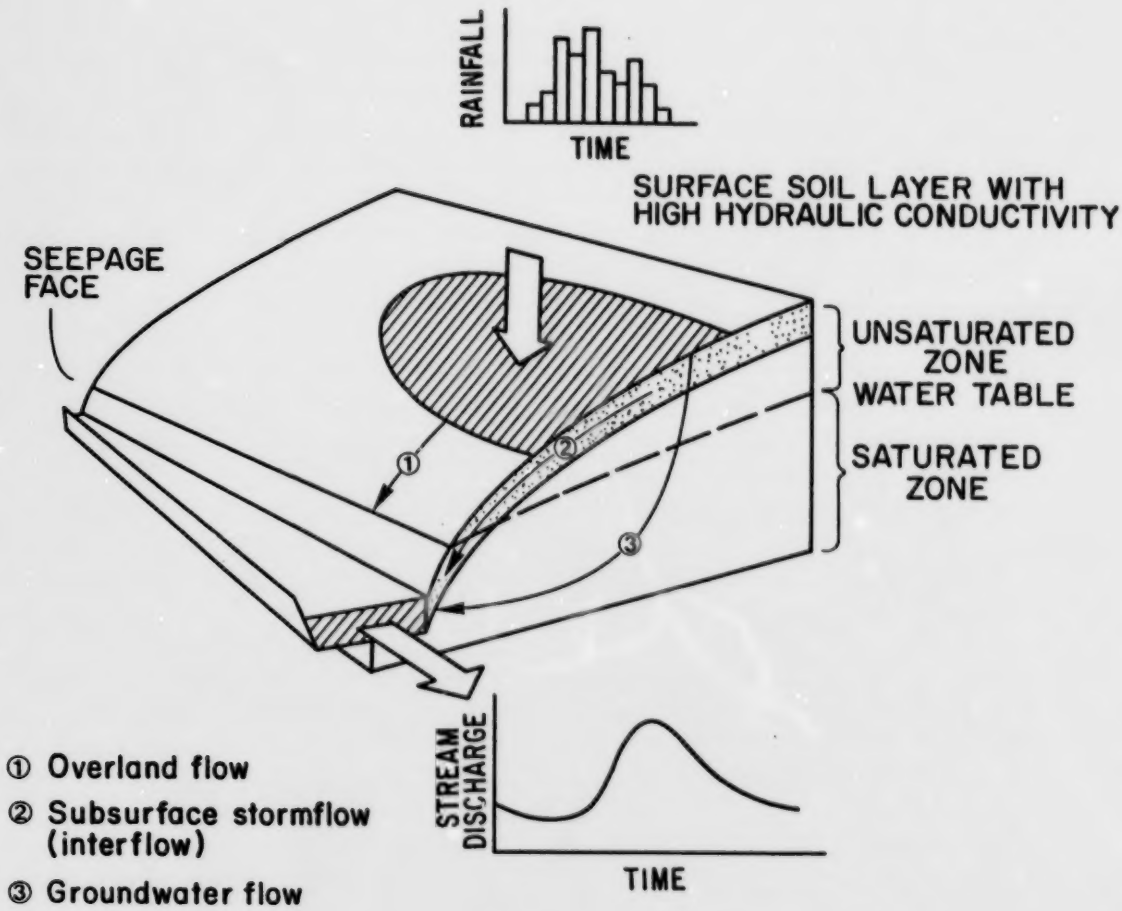

Figure 5. Mechanisms of delivery of rainfall to a stream channel from a hillslope in a small tributary watershed. Source: Freeze (1974)

is a relatively late occurrence in time and space, especially in humid, vegetated basins. Most overland flow hydrographs originate from small portions of the watershed that constitute no more than 10% and often as little as 1-3% of the basin area, and even on these restricted areas, only 10-30% of the rainfall events cause overland flow.

The second widely held concept of surface runoff generation promotes subsurface storm flow (or interflow) as a primary source of runoff. Hewlett and Hibbert (1963, cited by Freeze and Cherry 1979; 1967) showed the feasibility of such flow experimentally, and Whipkey (1965, cited by Freeze and Cherry 1979) measured lateral inflows to streams from subsurface sources in the field. The prime requirement is a shallow soil horizon of high permeability at the surface. There is reason to suppose that such surface layers are quite common in the form of the A soil horizon, or as agriculturally tilled soils or forest litter.

On the basis of simulations with a mathematical model of transient saturated-unsaturated subsurface flow in a two-dimensional hill slope cross-section, Freeze (1972) concluded that subsurface storm flow can become a quantitatively significant runoff component only on convex hillsides that feed deeply incised channels and then only when the permeabilities of the soils on the hill slope are in the very highest bracket of the feasibility range.

In many forested watersheds (Hewlett and Nutter 1970, cited by Freeze and Cherry 1979), a significant portion of the water arising from variable source areas arrives by means of subsurface stormflow. Figure 6 provides a summary of the various storm runoff processes in relation to their major controls.

Once moisture reaches the water table, it moves in response to a hydraulic gradient in a manner similar to water flowing in an open channel or pipe. However, the flow of groundwater is restricted by friction with the porous medium through which it flows. This results in low velocities and high head losses.

In relatively simple geological settings, the movement of groundwater can be quantified using the Darcy equation:

$$Q = KiA \qquad [6]$$

where Q = rate of flow
K = hydraulic conductivity
i = hydraulic gradient
A = area normal to the flow direction

The impact of topography on groundwater movement was described graphically by Hubbert (1940) and mathematically by Toth (1962,1963). Freeze and Witherspoon (1967) adapted the earlier analytical solutions to a digital model. As a result of the work by these four scientists, local, intermediate, and regional groundwater flow regimes have been recognized (Figure 7) and universally accepted by the scientific community.

Subsurface stratigraphy and the resulting subsurface variations in hydraulic conductivity can exist in an infinite variety. Geological heterogeneity can have a profound effect on regional groundwater flow. It can affect the interrelationship between local and regional systems, the surficial pattern of recharge and discharge areas, and the quantities of flow that are discharged through the systems.

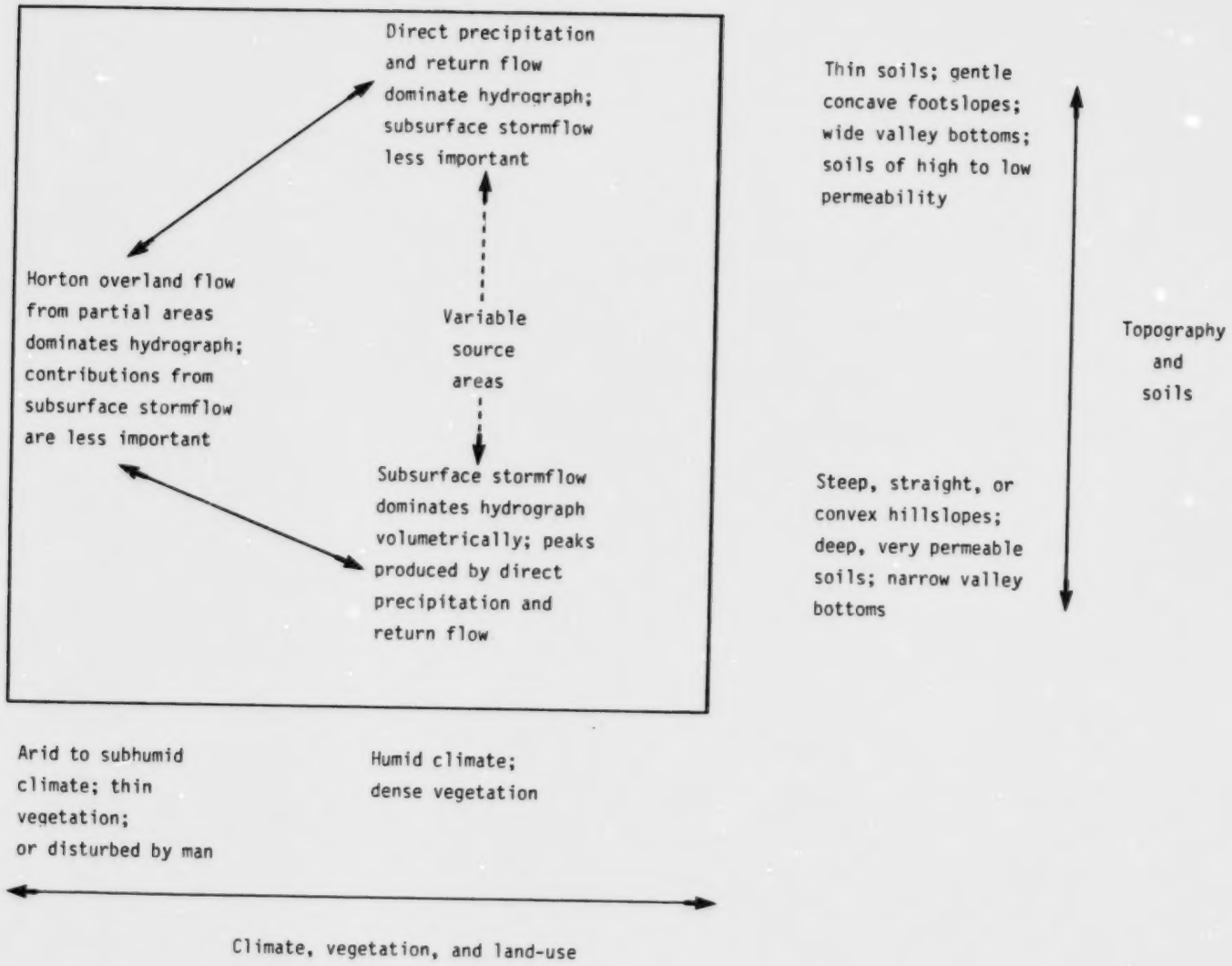
Direct precipitation and return flow dominate hydrograph; subsurface stormflow less important
Horton overland flow from partial areas dominates hydrograph; contributions from subsurface stormflow are less important
Variable source areas
Subsurface stormflow dominates hydrograph volumetrically; peaks produced by direct precipitation and return flow
Thin soils; gentle concave footslopes; wide valley bottoms; soils of high to low permeability
Topography and soils
Steep, straight, or convex hillslopes; deep, very permeable soils; narrow valley bottoms
Arid to subhumid climate; thin vegetation; or disturbed by man
Humid climate; dense vegetation
Climate, vegetation, and land-use

Figure 6. Illustration of the occurrence of various storm runoff processes in relation to their major controls. Source: Dunne (1978)

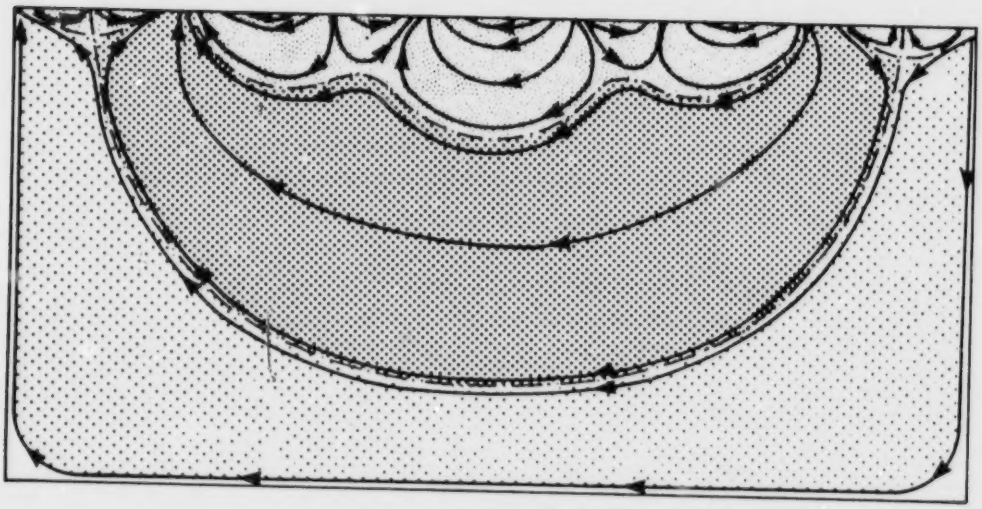
Region of local system of groundwater flow
Region of intermediate system of groundwater flow
Region of regional system of groundwater flow

Figure 7. Local, intermediate, and regional systems of groundwater flow. Source: Toth (1963)

In more complex geological settings, the Darcy equation tends to break down. In such situations, three dimensional groundwater flow is frequently modelled using the Laplacian equation:

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2} = 0 \qquad [7]$$

This equation forms the basis for both finite difference and finite element models that have been developed to examine groundwater flow conditions.

While the Laplacian type equations are acceptable for modelling steady or unsteady-state flow in a saturated medium, the following partial differential equation is used to describe transient flow through a saturated anisotrophic medium:

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) = S_s \frac{\partial h}{\partial t} \qquad [8]$$

In nature, the wide range in the variability of the parameters that influence groundwater movement results in very complex flow regimes. In addressing groundwater problems, care must be exercised in defining the flow regime, particularly when groundwater chemistry is a consideration.

There are three main approaches that can be used in studies of the processes of streamflow generation during storm runoff: (1) hydrometric monitoring using instruments such as current meters, rain gauges, observation wells, and tensiometers; (2) mathematical simulations; and (3) monitoring of dissolved constituents and environmental isotopes such as ^{2}H, ^{3}H, and ^{18}O.

Pinder and Jones (1969) used variations in Na^{2+}, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-} in their study of storm runoff components in small headwater basins in sedimentary terrain in Nova Scotia. In a similar investigation in Manitoba, Newbury et al. (1969) found SO_4^{2-} and electrical conductance to be the best indicators for identification of the groundwater component in that area. In these and many other investigations using the hydrochemical method, it is commonly concluded that the groundwater-derived component of streamflow during peak runoff is appreciable. Pinder and Jones (1969), for example, reported values in the range of 32-42%.

One of the main limitations in the hydrochemical method is that the chemical concentrations used for the shallow groundwater and to represent the direct runoff are lumped parameters that may not adequately represent the water that actually contributes to the stream during the storm. The chemistry of shallow groundwater obtained from wells near streams is commonly quite variable spatially. Direct runoff is a very ephemeral entity that may vary considerably in concentration in time and space.

To avoid some of the main uncertainties inherent in the hydrochemical method, the naturally occurring isotopes ^{18}O, ^{2}H, and ^{3}H can be used as indicators of the groundwater component of streamflow during periods of storm runoff. Fritz et al. (1976) utilized ^{18}O, noting that its concentration is very uniform in shallow groundwater and baseflow. Several studies utilizing stable isotopes have found that even during peak runoff periods, the groundwater component of the streamflow is considerable, often

as much as half to two-thirds of the total streamflow. Therefore, the understanding of the groundwater flow regime and geochemistry become inseparable from other factors influencing basin hydrology.

The geochemical evolution of groundwater has been widely studied and it is broadly accepted that the two major factors that influence the chemistry of groundwater are the mineralogy of the porous medium through which the water migrates, and the time during which the groundwater is in contact with the porous medium. It is obvious, therefore, that an understanding of groundwater flow regime is a prerequisite to an evaluation of groundwater chemistry in any particular area.

2.2 GEOCHEMICAL PROCESSES

The chemical interaction between infiltrating precipitation and geological materials has been intensively studied, and through the application of geochemical principles, it is possible to predict the evolution of the chemistry of groundwater.

2.2.1 General

As a result of chemical and biochemical interactions between groundwater and the geological materials through which it flows, and to a lesser extent because of contributions from the atmosphere and from surface water bodies, groundwater contains a wide variety of dissolved inorganic chemical constituents in various concentrations. A general classification of the inorganic species that occur in groundwater is shown in Table 1. The major naturally occurring ions in groundwater are Na^{+}, Mg^{2+}, Ca^{2+}, Cl^{-}, HCO_3^{-}, and SO_4^{2-}. The total concentration of these six major ions normally comprises more than 90% of the total dissolved solids in the water, regardless of whether the water is diluted or has a salinity greater than sea water (Freeze and Cherry 1979). The concentrations of the major, minor, and trace inorganic constituents in groundwater are controlled by the availability of the elements in the soil and rock through which the water has passed, by geochemical constraints such as solubility and adsorptions, by the rates of geochemical processes, and by the sequence in which the water comes into contact with the various minerals occurring in the geological materials along the flow paths. The most significant geochemical processes which influence the chemical quality of groundwater are: solution-precipitation; acid-base reactions; oxidation-reduction; ion exchange; adsorption-desorption; hydrolysis; and complexation.

As groundwater moves along its flow paths in the saturated zone, increases in total dissolved solids and most of the major ions normally occur. It is generally observed that shallow groundwater in recharge areas is lower in dissolved solids than water deeper in the same system, and is lower in dissolved solids than is water in shallow zones in the discharge areas. Chebotarev (1955), in a classic paper based on more than 10,000 chemical analyses of well water samples, concluded that groundwater tends to evolve chemically toward the composition of seawater. He observed that this evolution is normally accompanied by regional changes in dominant anion species, as indicated in Table 2. These changes occur as the water moves from shallow zones of active flushing through intermediate zones into zones where the flow is very sluggish and the water is old. This sequence, like many others in the geological sciences, must be viewed in terms of scale and geological setting with allowances for interruption and incompletion.

Table 1. Classification of dissolved inorganic constituents in groundwater.

Major constituents (greater than 5 mg/L)	
Bicarbonate	Silicon
Calcium	Sodium
Chloride	Sulphate
Magnesium	Carbonic acid

Minor constituents (0.01-10.0 mg/L)	
Boron	Nitrate
Carbonate	Potassium
Fluoride	Strontium
Iron	

Trace constituents (less than 0.1 mg/L)	
Aluminum	Molybdenum
Antimony	Nickel
Arsenic	Niobium
Barium	Phosphate
Beryllium	Platinum
Bismuth	Radium
Bromide	Rubidium
Cadmium	Ruthenium
Cerium	Scandium
Cesium	Selenium
Chromium	Silver
Cobalt	Thallium
Copper	Thorium
Gallium	Tin
Germanium	Titanium
Gold	Tungsten
Indium	Uranium
Iodide	Vanadium
Lanthanum	Ytterbium
Lead	Yttrium
Lithium	Zinc
Manganese	Zirconium

Source: Davis and De Wiest (1966)

Table 2. Chebotarev sequence.

Position along Flowpath	Anionic Composition of Groundwater	
	Primary Anion	Secondary Anion
Recharge area	HCO_3^-	—
	HCO_3^-	SO_4^{2-}
Increasing	SO_4^{2-}	HCO_3^-
Age	SO_4^{2-}	Cl^-
	Cl^-	SO_4^{2-}
Discharge Area	Cl^-	—

Crystalline rocks of igneous and metamorphic origin generally have at least one characteristic in common: they contain large amounts of quartz and aluminosilicate minerals such as feldspars and micas. In the soil zone, and in the groundwater zone to depths of many hundreds or thousands of metres, these minerals are thermodynamically unstable and tend to dissolve on contact with water. The dissolution processes cause the water to acquire dissolved constituents and the rock to become altered mineralogically.

As in the chemical evolution of groundwater in carbonate rocks, the dissolution of feldspars, micas, and other silicate minerals is strongly influenced by the chemically aggressive nature of water as caused by dissolved CO_2. When CO_2-charged waters that are low in dissolved solids encounter silicate minerals high in cations, aluminum, and silica, cations and silica are leached, leaving an alumina-silicate residue. This residue is usually a clay mineral such as kaolinite, illite, or montmorillonite. The cations released to the water are normally Na^+, K^+, Mg^{2+}, and Ca^{2+}. Another consequence of this process of incongruent dissolution is a rise in pH and in HCO_3^- concentration. Equations that describe these chemical changes in the water and rock, and interpretations of hydrochemical data from igneous and metamorphic rocks are shown in Table 3.

Groundwater contains dissolved gases as a result of: (1) exposure to the earth's atmosphere prior to infiltration into the subsurface environment; (2) contact with soil gases during infiltration through the unsaturated zone; or (3) gas production below the water table by chemical or biochemical reactions involving groundwater, minerals, organic matter, and activity. The most abundant dissolved gases in groundwater are N_2, O_2, CO_2, CH_4, H_2S, and N_2O. The first three make up the earth's atmosphere and, therefore, it is not surprising that they occur in subsurface water. CH_4, H_2S, and N_2O can often exist in groundwater in significant concentrations because they are products of biogeochemical processes that occur in non-aerated subsurface zones. Dissolved gases can have a significant influence on the subsurface hydrochemical environment.

2.2.2. Organics

Dissolved organic matter is ubiquitous in natural groundwater, although the concentrations are generally low compared to inorganic constituents. Organic compounds are those that have carbon and usually hydrogen and oxygen as the main elemental components in their structural framework. The species H_2, HCO_3^-, and CO_3^- are also important constituents in all groundwater but are not classified as organic compounds.

The chemical nature of organic material in groundwater is not well understood. However, investigations of soil water suggest that most dissolved organic matter in subsurface flow systems is in the form of fulvic and humic acid. These acids are organic compounds that persist in subsurface waters because they are resistant to degradation by microorganisms. The generation of humic acid in acidic soils has the peculiar distinction of more strongly acidifying the environment than do the final oxidation products of CO_2 and H_2 (Krug and Frink 1983b). Although less is known about the origin and composition of organics in groundwater as compared to inorganic constituents, analyses of the total concentrations of dissolved organic carbon (DOC) commonly show concentrations in the range of 0.1 to 10 mg/L.

Table 3. Reactions for incongruent dissolution of some aluminosilicate minerals. Solid phases are underlined.

Gibbsite-kaolinite	$\underline{Al_2O_3 \cdot 3H_2O} + 2Si(OH)_4 = \underline{Al_2Si_2O_5(OH)_4} + 5H_2O$
Na-montmorillonite-kaolinite	$\underline{Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2} + 1/3H^+ + 23/6H_2O = \underline{7/6Al_2Si_2O_5(OH)_4} + 1/3Na^+ + 4/3Si(OH)_4$
Ca-montmorillonite-kaolinite	$\underline{Ca_{0.33}Al_{4.67}Si_{7.33}O_{20}(OH)_4} + 2/3H^+ + 23/2H_2O = \underline{7/3Al_2SiO_2O_5(OH)_4} + 1/3Ca^{2+} + 8/3Si(OH)_4$
Illite-kaolinite	$\underline{K_{0.6}Mg_{0.25}Al_{2.30}Si_{3.5}O_{10}(OH)_2} + 11/10H^+ + 63/60H_2O = \underline{23/20Al_2Si_2O_5(OH)_4} + 3/5K^+ + 1/4Mg^2 + 6/5Si(OH)_4$
Biotite-kaolinite	$\underline{KMg_3AlSi_3O_{10}(OH)_2} + 7H^+ 1/2H_2O = \underline{1/2Al_2Si_2O_5(OH)_4} + K^+ + 3Mg^{2+} + 2Si(OH)_4$
Albite-kaolinite	$\underline{NaAlSi_3O_8} + H^+ + 9/2H_2O = \underline{1/2Al_2Si_2O_5(OH)_4} + Na^+ + 2Si(OH)_4$
Albite-Na-montmorillonite	$NaAlSi_3O_8 + 6/7H^+ + 20/7H_2O = \underline{3/7Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2} + 6/7Na^+ + 10/7Si(OH)_4$
Microcline-kaolinite	$\underline{KAlSi_3O_8} + H^+ + 9/2H_2O = \underline{1/2Al_2Si_2O_5(OH)_4} + K^+ + 2Si(OH)_4$
Anorthite-kaolinite	$\underline{CaAl_2Si_2O_8} + 2H^+ + H_2O = \underline{Al_2Si_2O_5(OH)_4} + Ca^{2+}$
Andesine-kaolinite	$\underline{Na_{0.5}Ca_{0.5}Al_{1.5}Si_{2.5}O_8} + 3/2H^+ + 11/4H_2O = \underline{3/4Al_2Si_2O_5(OH)_4} + 1/2Na^+ + 1/2Ca^{2+} + Si(OH)_4$

2.3 pH AND ACIDIFICATION PROCESSES

2.3.1 The pH Scale

The relative concentration of hydrogen ions in water indicates whether the water will act like a weak acid or if it will perform as an alkaline solution. When the amount of hydrogen ions is excessive in relation to the other ions in the solution, an acid reaction results.

The hydrogen ion concentration of water is expressed by its pH value. A pH value of 7 indicates a neutral solution, neither alkaline nor acid. A pH of less than 7 indicates an acidic condition; a pH value greater than 7 indicates an alkaline solution. A water molecule (H_2O), has a slight tendency to break down into ions the same way in which some of the dissolved minerals are ionized. When water ionizes, it divides into a positive hydrogen ion (H^+) and a negative ion called the hydroxyl ion (OH^-). In pure water, a small proportion of the molecules are ionized in this way. In pure water, the concentration of hydrogen ions per litre of water is expressed by a pH value of 7. The scale of pH values is such that a change of one pH unit represents a 10-fold change in H^+ ion concentration. For example, suppose that a small quantity of acid added to distilled water changes the pH to 6. This means that the number of H-ions has been increased 10 times by the addition of the acid. Similarly, a water with a pH value of 8 has only 1/10 as many H-ions as distilled water and a pH value of 9 represents only 1/1000 as many as at the neutral value of 7. The number of negative OH ions changes in the opposite fashion. Thus, water with a pH value of 9 has 100 times more OH ions than neutral water with pH value of 7. The OH ions give water its alkaline reactions; therefore, water with a pH of 9 would be quite alkaline.

2.3.2 Groundwater Acidification Processes

The pH value of most groundwaters is controlled by the amount of dissolved carbon dioxide gas and the dissolved carbonates in the mineral salts. Carbon dioxide gas (CO_2) dissolved in water forms carbonic acid.

The reaction of CO_2 and water can be represented by [9] and [10] below, and these are summed to obtain [11] (Reuss 1975):

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad [9]$$

$$H_2CO_3 \longrightarrow H^+ + HCO_3^- \qquad [10]$$

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3^- \qquad [11]$$

In distilled water, a small amount of this weak acid lowers the pH appreciably. We expect a pH of 5.65 for pure rain water in equilibrium with atmospheric CO_2. Throughout geological history, one of the important roles of geological materials at the earth's surface has been the consumption of naturally occurring atmospheric acid, so the advent of the contemporary "acid rain" is not an entirely new or unfamiliar phenomena.

For geological materials that have very low carbonate contents, H^+ neutralization is effected essentially by a 2-step process (Kramer et al. 1979, cited by Wyatt 1984; Johnson et al. 1981; and Jackson and Patterson 1982). The process begins when the geological material comes in contact with water of pH <4.5. The H^+ acidity will

initially be consumed by the rapid dissolution of soil zone hydrous aluminum and iron oxides, and by exchange with cations electrostatically bound to mineral surfaces. This step is followed by a second stage involving the dissolution of trace amounts of calcite and the less rapid dissolution of aluminosilicate minerals. If the pore water is in contact with the sediment long enough to be involved in the second acid neutralization step, then the pH may rise enough to cause dissolved Al and Fe to precipitate back out of solution as hydrous oxides. Indeed, for carbonate-rich glacial deposits and their derived soils, the dissolution of carbonate minerals to produce bicarbonate ions becomes the singly most effective acid neutralizing reaction and raises the pH quickly enough that the other neutralization reactions are largely bypassed. In this sequence the contribution of each mineral reaction towards the acid neutralizing capacity of a sediment can be dependent on the type, abundance, and size fractionalism of each reactant, and the initial pH and residence time of the surrounding pore water (Wyatt 1984).

Because the water that circulates through the groundwater zone is generally isolated from the earth's atmosphere, oxygen that is consumed by hydrochemical and biochemical reaction is not replenished. For reduction of inorganic constituents to occur, some other constituents must be oxidized. The oxidized compound is generally inorganic matter. To illustrate the process of organic matter oxidation, a simple carbohydrate (CH_2O) will serve as the organic material. Numerous other compounds such as polysaccharides saccharides, fatty acids, amino acids, and phenols may be the actual organic compound involved in the reaction.

$$1/4\ CH_2O + 1/4\ H_2O = 1/4\ CO_2(g) + H^+ + e \qquad [12]$$

This half reaction combined with the half reaction for reduction of an inorganic compound,

$$1/4\ O_2 + H^+ + e = 1/2\ H_2O \qquad [13]$$

yields the redox relation

$$O_2(g) + CH_2O = CO_2(g) + H_2O \qquad [14]$$

which represents the process of organic matter oxidation in the presence of bacterial and free molecular oxygen. This redox process is the main source of dissolved CO_2. Carbon dioxide combines with H_2O to produce H_2CO_3 which geochemically is an acid of considerable strength. Because the solubility of O_2 in water is low (9 mg/L at 25°C) and because O_2 replenishment in subsurface environments is limited, oxidation of only a small amount of organic matter can result in consumption of all the dissolved O_2. O_2 consumption and CO_2 production is, therefore, a widespread process in the very shallow part of the subsurface environment.

In many groundwater systems the H^+ ions produced by redox reactions are consumed by reaction with minerals. The pH, therefore, does not decrease appreciably. As the acid buffering ion exchange reaction in the humus layer is slow, influence of the underlying mineral soil is of less importance here than in other places. This is not

because the bedrock, moraines, and tills consist of so-called "acid rocks" as many people tend to believe. The concept "acid rocks" (gneisses and granites) does not mean that they result in pH values below 7 when reacting with water. On the contrary, rock, even quartzitic gneisses (with a low content of feldspars), consumes protons and produces alkaline leachates when percolated by rainwater. There is no great difference in the final pH of the water phase seeping through soils from "acid rocks" and from "basic rocks." In both cases, the pH will end up to be approximately 8. The time necessary for neutralization in a mineral soil is, however, fairly long (several days and weeks) (Rosenqvist 1978).

According to Hem (1970), most groundwaters have pH values ranging from about 6.0 to a little over 8.5. Those groundwaters with pH values below approximately 4.5 probably contain free mineral acids from mine waters, volcanic gases, or from anthropogenic sources. Moderately low pH values may be associated with small amounts of mineral acids from sulphide sources or with organic acids.

Rosenqvist (1978) concluded that the acidity of soil leachate and resulting acidic water was a factor determined more by patterns of land use than by acidic precipitation. Although this theory has been disputed by the work of Drablos and Tollan (1980) in Norway, there is little doubt that land use and vegetation type influence the acidity of soil leachates and groundwater chemistry.

2.3.3 Atmospheric Acidification Processes

Recent environmental phenomena have focussed scientific attention on the subject of "acid rain." In the normal context, "acid rain" refers to acids that form in the atmosphere from the input of SO_4 and NO_4 from anthropogenic sources. It has been recognized by the scientific community for a number of years that precipitation normally is somewhat acidic as a result of the solution of atmospheric CO_2. Similarly, the reaction of SO_2 and NOx (whether in gaseous or dry form) with water results in the formation of sulphuric and nitric acids. These acids may enter the land based portion of the hydrologic cycle as either precipitation or dry deposition.

Emission of sulphur into the atmosphere occurs mainly as particulate S and gaseous SO_2. In the atmosphere, this leads to increased concentrations of H^+ and SO_4^{2-} in rain and snow:

$$S + O_2 \longrightarrow SO_2\ (g) \qquad [15]$$

$$SO_2\ (g) + H_2O + 1/2\ O_2 \longrightarrow SO_4^{2-} + 2H^+ \qquad [16]$$

It has been inferred that atmospheric pH values of less than 5.6 result from the presence of strong acids in the environment, notably H_2SO_4 and HNO_3, and to some extent, HCl. Major cations commonly encountered in atmospheric deposition include Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^{4+}. Excluding HCO_3 and H^+, the excess of anions over cations on an equivalent basis may be used to estimate net atmospheric acidity as shown (Reuss 1975):

$$e = 2\ [SO_4^{2-}] + [NO_3^-] \text{ and } [Cl^-] - 2\ [Ca^{2+}] - 2\ [Mg^{2+}] - [K^+] - [NH_4^+] \qquad [17]$$

where e = excess acid in moles per litre (-e = alkalinity).

2.3.4 Terrestrial Acidification Processes

The widespread acidification of the environment has been documented for several years. Modification of the ambient pH conditions of the environment have caused several changes in the biological balance of the ecosystem. Much of the attention has focussed on atmospheric loading, and on surface water and forest response to acidification. On the other hand, the extent of acidification of the groundwater is still largely unknown. Discussions of the interaction of acid precipitation with the terrestrial environment have tended to concentrate on near surface soil horizons and vegetation responses. Few studies have considered the rates that deeper seated, groundwater movement plays in the acidification process. It was recognized that the acidic input into soil-rock-water systems can be neutralized if sufficient buffering agents are present and if the rate of neutralization can balance the rate of acidic input. With time, consumption of buffering agents by the various neutralization processes leads to an exhaustion of the neutralizing ability of the soil-rock-water system and to a lowering of the pH value within the system. Much of the early work therefore focussed on the potential acidification of groundwater as reflected by pH. In attempting to quantify acidification or potential acidification, scientists have also used a wide range of other chemical parameters or descriptors. The major acidity descriptors include:

1. pH = negative log of hydrogen ion concentration;
2. Alkalinity = sum of concentration of Ca and concentration of Mg;
3. Cation Exchange Capacity (CEC) = sum of exchangeable base cations and acidity;
4. Buffering Capacity = amount of acid or base required to change the pH of a given quantity of soil by one or more pH units;
5. Calcite-Saturation Index (CSI) = incorporation of measurements of both alkalinity and pH;
6. Acid Neutralization Capacity (ANC) = equal to H^+ initial + H^+ added - H^+ final; and
7. Lime Potential (LP) = pH - ½ p (Ca, Mg).

As well as this wide range of descriptors, Last et al. (1980) recognized a number of neutralization processes that take place in the subsurface, not all of which are tied to the consumption of $CaCO_3$:

1. H^+ ions are consumed by the dissolution of $CaCO_3$: carbonic acid/carbonate buffer range (pH 6.2-8.6),
2. H^+ ions are consumed by the weathering of silicates: carbonic acid/silicates buffer range (pH 5.0-6.2),
3. H^+ ions are consumed by dissolving AlOOH from weathered silicates with the formation of polymeric Al-hydroxo-cations: cation exchange buffer range (pH 4.2-5.0),
4. H^+ ions are consumed by formation of Al^{3+} ions from polymeric Al-compounds: aluminum buffer range (pH 3.0-4.2),
5. H^+ ions are consumed by the formation of Fe ions from iron/oxides: iron buffer range (pH less than 3.5 to 3.0).

While these lists are not all-inclusive, they do provide an indication that the chemical processes of acidification are complex, and cannot be adequately described by single ion responses.

The ground receives increments of acid in part through atmospheric deposition and in part through certain processes in the ground itself. It is natural, therefore, for groundwater near the surface to be weakly acidic until there has been time for the minerals in the ground to neutralize it.

2.3.5. Evidence of Groundwater Acidification in Nordic Countries

pH values between 5 and 6 occur in groundwater throughout Sweden (Hultberg and Johansson 1981; Jacks and Knutsson 1981, cited by Swedish Ministry of Agriculture 1982). In the southwestern parts of the country, pH values between 4 and 5 have been recorded in shallow wells. There have been additional cases of pH measurement below 4. The results of a limited inventory of acid groundwater in Sweden are shown in Figure 8. The inventory shows that the pH of groundwater in shallow wells is consistently lower than the pH in deeper, drilled wells. In the provinces of Holland, Bohuslan, Alusborg, Varmland, Orebra, and Bleking, the percentages of shallow wells with pH <6.0 are 66%, 76%, 41%, 43%, 39%, and 31%, respectively. In Laholm district of Holland, 58% of the shallow wells have pH <6.0 (Hultberg and Johansson 1981).

Groundwater from drilled wells was demonstrated to be generally less acidic. The percentages of drilled wells with pH <6.0 were 35%, 10%, 5%, 13%, and 26% in the four provinces of Bohuslan, Varmland, Orebra, Bleking, and the district of Laholm, respectively (Hultberg and Johansson 1981).

In the southern part of the province of Bohuslan, where the most widespread problem with acidic groundwater was observed, 49% of the shallow wells had a pH <5.5, while only 13% of the drilled wells had such a low pH. In this study, pH in shallow wells decreased with increased height of the well above sea level. A similar effect was earlier described for acidic lakes in the same area. pH of the well water was also shown to decrease with decreasing depth. Wells in highly permeable ground such as sand and gravel generally had the lowest pH values. Moraines with varying texture generally showed low but more varying pH. Shallow wells in clayey (marine) soil often had high pH values but the average pH was just over 6.0 in Bohuslan (Figure 9).

Compared with the data from shallow wells, it is seen that even deep large groundwater aquifers have gradually been acidified in southern Sweden (Hultberg and Johansson 1981).

Henricksen and Kirkhusmo (1982) noted that in Norway, where the pH of groundwater is acidified to the 5.0-5.5 range, the bicarbonate buffer is almost exhausted. If the source of the groundwater acidity is, in fact, from atmospheric deposition, it may be concluded that if atmospheric loading were to continue at elevated concentrations, the buffering capacity of the soil surface material would ultimately be depleted and more significant acidification of the subsurface would occur.

Groundwater acidification is in many cases a slow process, but nevertheless, some 18,000 lakes with inflow of both surface and groundwater are already affected in Sweden (Swedish Ministry of Agriculture 1982).

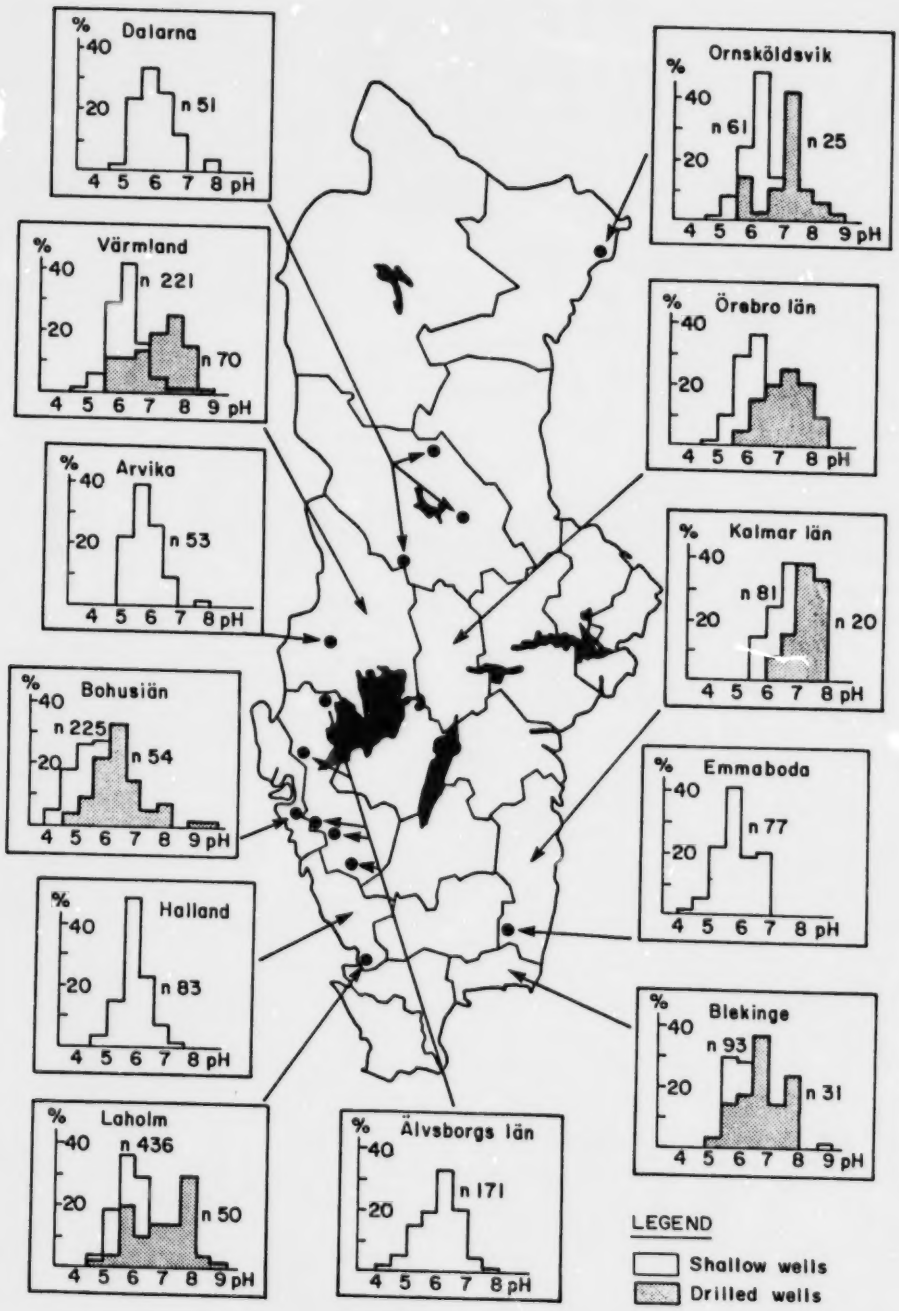

Figure 8. Partial inventory of acid groundwaters in Sweden. Source: Jacks and Kucera (1982)

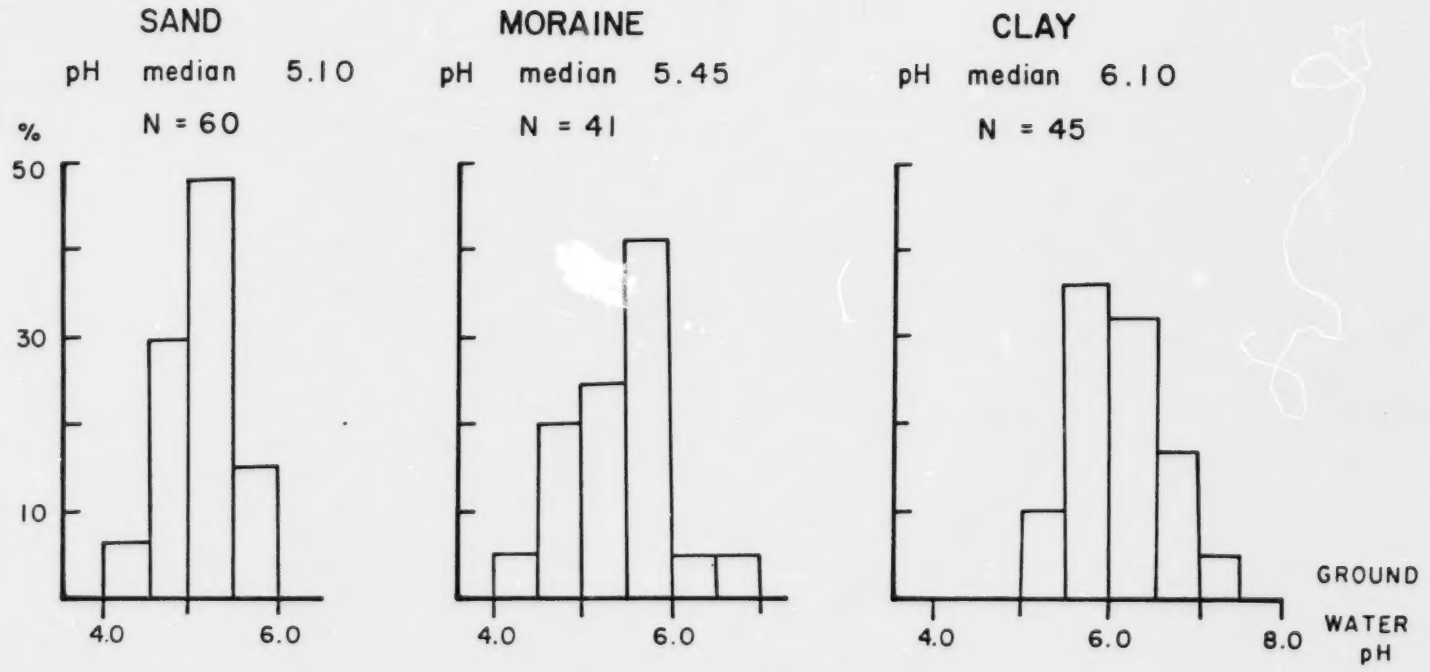

Figure 9. pH in groundwater from shallow wells (1-10 m) in different soil types (Bohuslan). Source: Hultberg and Johansson (1981)

Most of the acidic Swedish lakes are in areas with rocks that do not weather easily (gneiss, granite) and soils that are low in lime. In the initial stage of an oligotrophic lake in this geological setting, the pH value is 6-7, the water is decidedly low in nutrients, and the animal and plant life is limited. Susceptibility to acidification is therefore relatively high from the outset, in contrast to that of lakes in lime-rich regions. Sweden's most tolerant lake areas are found in Skane, parts of Ostergotland and Vastergotland, Uppland and Jamtland, and on the islands of Oland and Gotland. In these areas, the bedrock is lime-rich or the soil is calcareous and, thus, has a naturally high content of buffering bicarbonate ions. In consequence, the water is neutral to slightly alkaline, with pH values between 7 and 8. The nutrient-rich water supports thriving plant and animal life.

In several Swedish watersheds, hydrological research shows that the bulk of the lake water has passed through the ground (Rodhe 1980). It has been concluded that if lakes in an area have been acidified, the groundwater nearest the surface must have been affected by the acidification process. In Bohuslan, it has been possible to establish a direct relationship between acidic groundwater and acidic lake water.

Sensitive fishes in Swedish waters are the roach, the minnow, and the salmon. Populations of these species decline when the pH goes below 6. Pike and perch are hardier; they can tolerate a pH down to 5.0. Before the roach gets to the point of complete extinction, its normal reproductive capacity is so seriously impaired that no new generation of roach are born. When they die, the entire stock dies with them.

The fish sometimes die even in lakes which still have moderate pH values. This is also a consequence of acidification and is due to aluminum poisoning. The solubility of aluminum increases when the pH falls. The metal is most poisonous at a pH just above 5, being precipitated in the form of aluminum hydroxide on the gills of the fish. The fish survive longer in brownish water high in humus than in clear lakes, the reason being that the humus substances fix the aluminum so that it is no longer toxic (Muniz 1981, cited by Johansson and Nyborg 1981).

The Nordic Hydrological Program (1982) has disagreed with those conclusions cited above, that there is good evidence for groundwater acidification. The Program has concluded, instead, that it has not yet been possible in the Nordic countries to show decreasing trends in the pH values of groundwater. However, they conceded that if the acidification of the environment continues, it will eventually lead to acidification of the groundwater, although most likely with a delay greater than is the case for acidification of surface water. The mass media has, in general, given the public the impression that groundwater acidification is a fact within large areas. The NHP feels that the investigations cited above describe only the present situation, and cannot determine whether the groundwater quality is worsening or improving; historical trends must be incorporated to make such conclusions.

It is this author's opinion that the criticisms of the Nordic Hydrological Program are not totally substantiated. Evidence of temporal changes in groundwater chemistry indicating acidification has been presented (Hultberg and Wenblad 1980; Aastrup et al. 1981, Jacks and Knutsson 1981, and SNV 1981, cited by Swedish Ministry of Agriculture 1982; and Soveri 1982). Also, an inverse relationship between SO_2 loading and groundwater alkalinity has been observed in at least one major aquifer in Sweden. Changes

in bicarbcnate, calcium, magnesium, and sulphate concentrations have been found in areas receiving acid precipitation. The study of groundwater in this respect has been hampered by the short time span for which data are available, and the areal heterogeneity of the data. In general, the groundwater in the Nordic countries has relatively low pH values in the shallow aquifers in glaciofluvial deposits and till within areas with acid to intermediate rocks. These groundwaters are therefore sensitive to relatively small increases in acid input.

The denial of increasing acidic groundwater conditions in the Nordic countries does not stand up to scrutiny. The evidence of acidic conditions in groundwater is significant. It must be recognized that acidification of groundwater can be a naturally occurring phenomena. Therefore, the question really is: "To what extent has atmospheric deposition contributed to the acidification of groundwaters?" Krug and Frink (1983b) and Rosenqvist (1978) have previously concluded that land use practices have played a more significant role in soil and groundwater acidification than has atmospheric deposition.

2.3.6 Evidence of Groundwater Acidification in North America

In response to heavy atmospheric loading in central Ontario and the acidification of lakes in that area, the Ontario Department of Environment undertook a survey of existing water wells to determine the possible impact of acidification on domestic and municipal groundwater supplies (Sibul and Vallery 1982; Sibul and Reynolds 1982).

Approximately 2000 chemical analyses were reviewed and groundwater pH values were noted for samples obtained in the Shield area. Most (lab) pH values were well above 6, and many above 7; however, some pH values were found to be between 5 and 6. These results suggested that groundwater pH values are usually above 6, whether in an area receiving light or heavy loading of acid precipitation, and that the effects of acid precipitation, if present, are not producing widespread, low pH values (Figures 10 and 11).

It appears that site specific factors of hydrogeology, composition of overburden and bedrock materials, and precipitation chemistry interact to form complex physical and chemical environments that determine the ultimate groundwater pH values. Appreciating that groundwater pH's likely change along the flowpath to maintain equilibrium with a variety of soil chemistries and precipitation quality, an attempt to explain differences in the hydrochemical systems may be achieved only through intensive, site specific studies well beyond the scope and purpose of the present investigation.

Although it is difficult to determine spatial trends of pH's in Figure 10, the more frequent occurrence of pH values of less than 6.0 just southeast of Bracebridge is apparent. Most of the pH values of less than 6.0 occur in relatively shallow wells. This relationship between well depth and acidity is similar to the observations made in Sweden. On the other hand, not all shallow wells have pH values of less than 6.0 and this likely reflects the modification of infiltrated acid rain by overburden and bedrock chemistry (Figure 11).

In the Sudbury area, of a total of 125 sampling sites, 123 represented private domestic wells and two sites (at Capreol and Hamner) represented groundwater municipal supplies. Results of the survey indicated a range of water quality in which 6 sites (5%) had pH values equal to or less than 6.0, 54 sites (43%) had pH values between 6.0 and

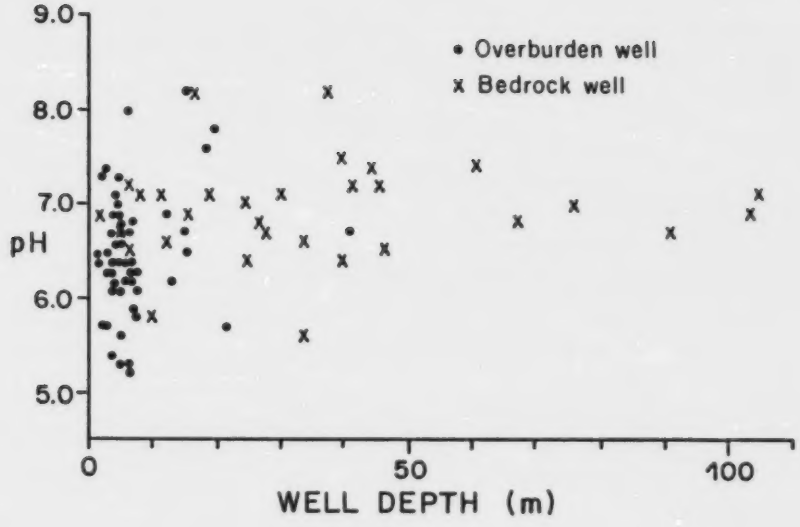

Figure 10. Groundwater pH values and well depths. Source: Sibul and Vallery (1982)

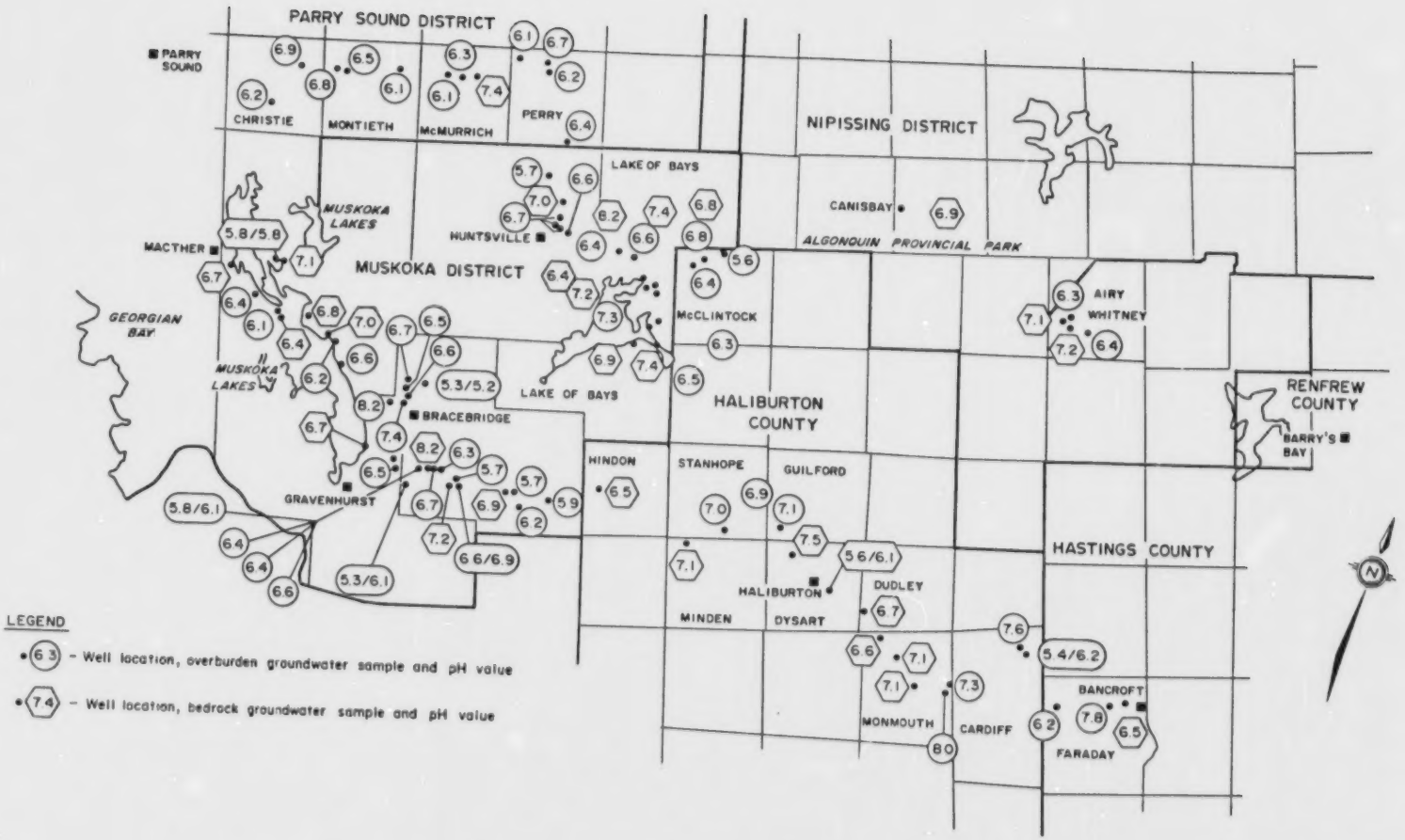

Figure 11. Distribution of groundwater pH values.

7.0, and 65 sites (52%) had pH values equal to or greater than 7.0. Only one site had a pH value less than 5.

Because of the demonstrated dependence of pH and CO_2, it would appear that acid precipitation has not affected groundwater to a great extent in the Muskoka and Sudbury areas of Ontario. However, this may change in the future as suggested by groundwater data in Sweden, where in some areas groundwater pH values attributed to acid precipitation have frequently been found to be less than 5. With basically similar geology, and if acid loading conditions remain at present levels, it is reasonable to expect a greater degree of acidification of groundwaters in Ontario in the future.

The ILWAS study executed in Panther Lake, Woods Lake, and Sagamore Lake basins in the Adirondacks of New York State observed increasing pH levels with increased depth of sampling similar to the trends observed in Sweden (Chen et al. 1983)(Figures 12 and 13).

2.4 CHANGES IN CONCENTRATION OF MAJOR IONS

The composition of water flowing through and out of soils and bedrock largely reflects the composition of the material that the groundwater has passed through. The chemical processes involved are mainly relatively rapid cation exchange reactions with soil colloidal materials, and slow acid hydrolysis reactions which decompose primary minerals (Bache 1984).

Under normal conditions, the natural leaching processes, which have been going on for thousands of years and which are still active, will lead to a reduction of the acid neutralization capacity of soil, surficial deposits, and bedrock.

The major chemical constituents that are involved in this leaching process are, of course, dependent upon the chemistry of the rock material; however, the major cations and anions may include: calcium, magnesium, sodium, potassium, carbonate-bicarbonate, sulphate, chloride, and nitrate.

It is recognized at the outset that acid precipitation results in certain chemical constituents being leached into the land based portion of the hydrologic cycle. The constituents commonly present in acidic atmospheric deposition include sulphate, nitrate/nitrite and a variety of metals in lesser quantities. In assessing the impact of atmospheric deposition on groundwater geochemistry, two basic questions must be addressed:

1. To what extent is the addition of chemical mass from the atmosphere reflected in the chemistry of groundwater?
2. To what extent does the addition of atmospheric acidity alter the geochemical processes that are active in the subsurface?

2.4.1 Cations

The effect of acidic deposition on geochemical processes and ultimately on the ionic chemistry of groundwater has received relatively little attention from researcher. In the mid-1970's, it was observed in Sweden (Aastrup et al. 1981, cited by Swedish Ministry of Agriculture 1982) that calcium (hardness) (Figure 14) increased in groundwater acidified by atmospheric deposition. At the same time, alkalinity as measured by

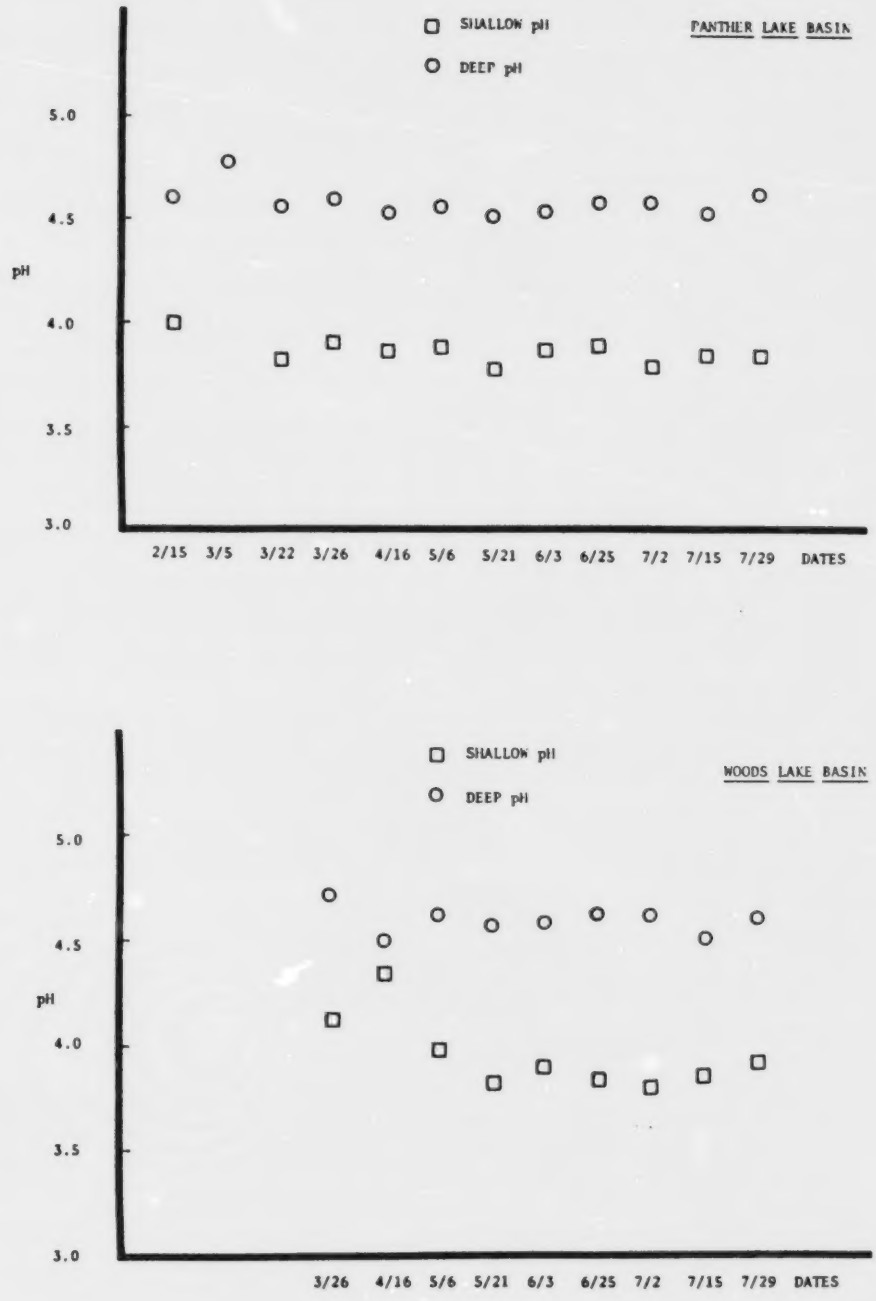

Figure 12. Average solution pH values for shallow and deep lysimeters in the Panther and Woods Lake basins. Source: Cronan (1983)

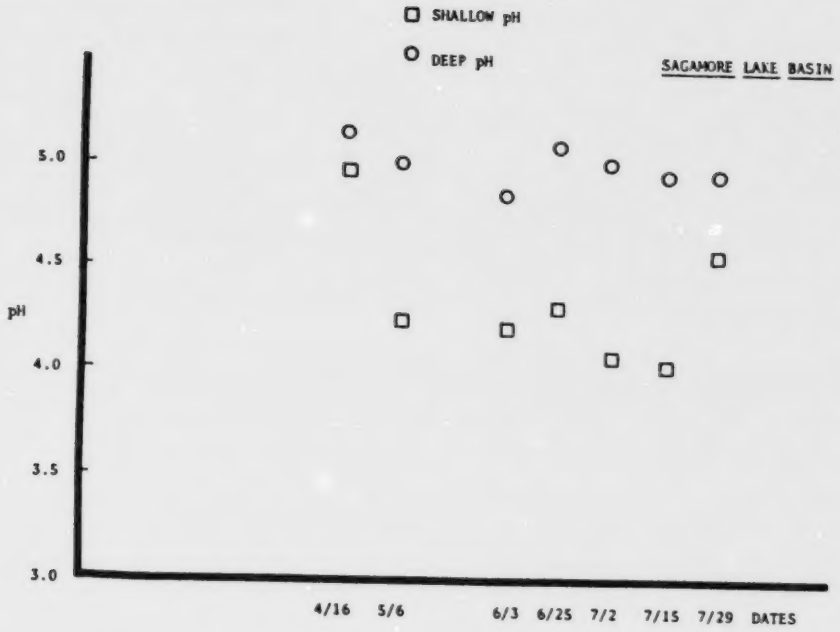

Figure 13. Average solution pH values for shallow and deep lysimeters in the Sagamore Lake basin. Source: Cronan (1983)

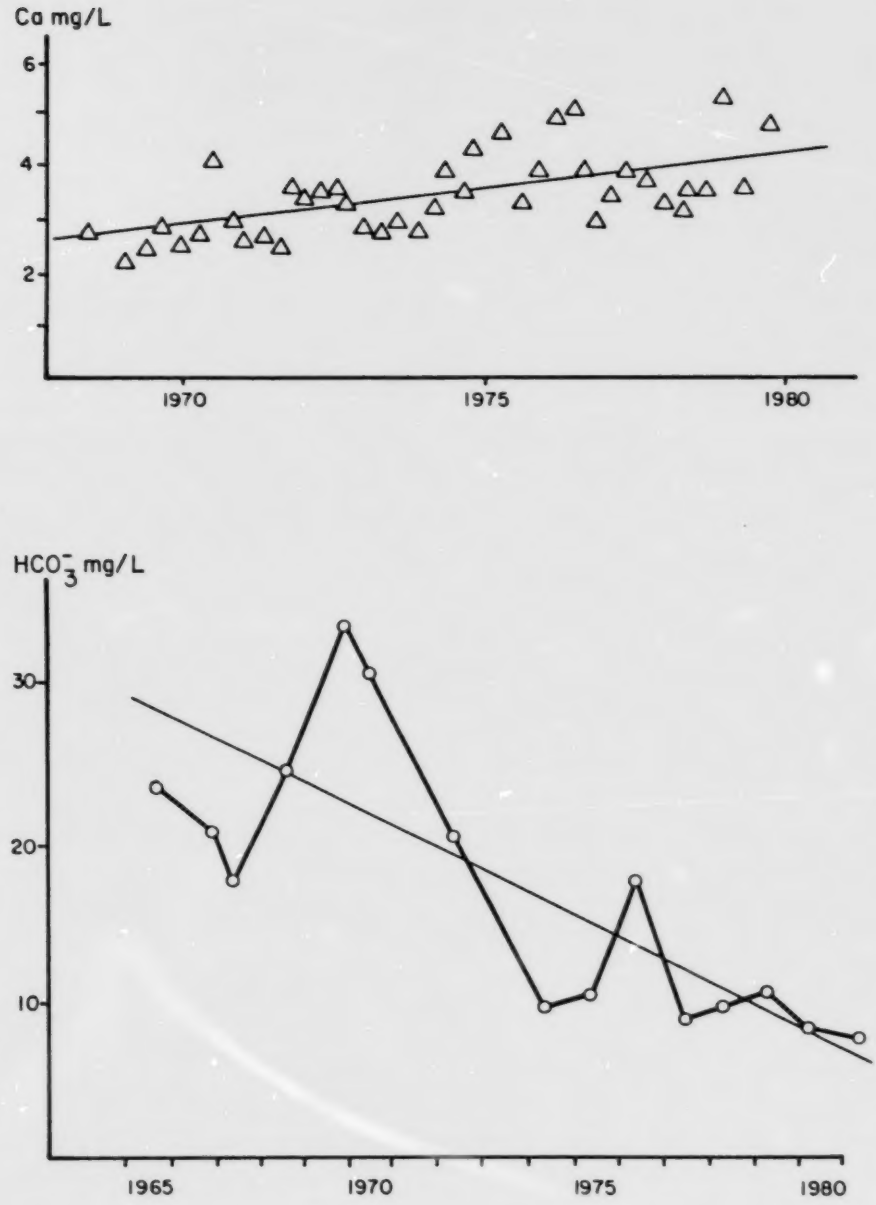

Figure 14. Changes in calcium content and alkalinity in municipal groundwater in Sweden. Source: Jacks and Knutsson (1981)

HCO_3^- was observed to be decreasing. In Norway, increases in calcium and magnesium concentrations were observed in groundwater in areas suffering from acidic deposition. Hultberg and Johansson (1981) have been unable to document an inverse relationship between pH of groundwater and concentrations of Ca, Mg, and K (Figure 15). Hultberg and Wenblad (1980) stated that calcium and bicarbonate in groundwater (in Sweden) usually have the same origin, and in groundwater unaffected by acidic deposition they can be expected to show more or less the same variation. In groundwaters affected by acids, the bicarbonate concentration is often decreasing (Figure 14) while the calcium concentration may be expected to increase because of the weathering process accelerated by the acidic deposition. Note in Figure 16 that pH remains essentially unchanged while alkalinity declines dramatically.

Similar increases in Ca, Mg, K, and Na were observed in soil leachates by Sparks and Curtis (1983) (Figures 17, 18, 19, and 20) and Lee and Weber (1982) when acidic water was added to selected soil profiles.

2.4.2 Anions

Regional studies of the effects of acidic deposition on groundwater were performed in the Scandinavian countries. Studies of chemical analysis from municipal groundwater sources (Figure 14; Jacks and Knutsson 1981, cited by Swedish Ministry of Agriculture 1982) and data from the groundwater network of the Geological Survey of Sweden (Aastrup et al. 1981, cited by Swedish Ministry of Agriculture 1982) revealed that in spite of a wide range in temporal variability there are definite changes occurring in the hardness and sulphate content of the groundwater; the hardness is increasing, the sulphate content is increasing, and the alkalinity is often decreasing.

2.4.2.1 Alkalinity. In the mid-1970's, high levels of sulphur dioxide emissions at Karlshamm, Sweden were related to a lowering of the alkalinity of municipal groundwater sources in the vicinity (SNV 1981, cited by Swedish Ministry of Environment 1982). Since the emissions were reduced, the alkalinity has increased to the concentrations observed in the pre-1970's. Only the water wells completed in bedrock have shown dramatically depressed alkalinity values after 1975. The remaining wells do not show a long-term trend towards the depletion of alkalinity. It is inferred from the data that the depression in alkalinity in 1975 may have resulted from temporary perturbation of other factors influencing the hydrologic regime. This does not imply that acidic deposition was not a factor in the drop in alkalinity, but that other factors as well have a major influence in the manner in which acidic deposition interacts with the groundwater regime (Figure 21).

To investigate if large municipal groundwater aquifers are undergoing long-term acidification, annual analyses covering from 7 to 23 years were compiled from nine municipal supplies in highly permeable (sand, gravel) soils (Martensson 1981, cited by Hultberg and Johansson 1981; Hultberg and Wenblad 1980). With few exceptions, the pH's were below 6 and no significant changes were indicated. However, the alkalinity had decreased in seven of the nine aquifers. In five of the aquifers the decrease in alkalinity was statistically significant during a 10-15 year period. In some cases the bicarbonate concentrations were halved during this period. Similarly, a significant

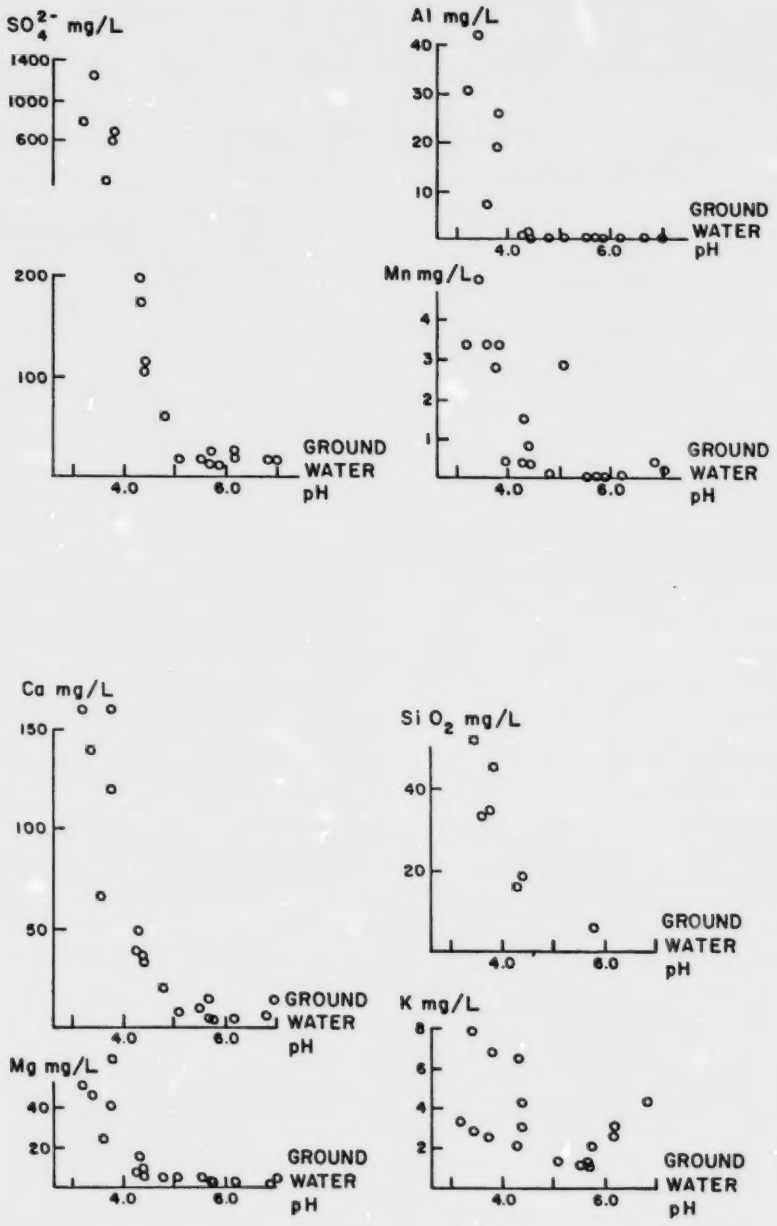

Figure 15. Concentrations of calcium, magnesium, silica, and potassium in relation to pH in acidified groundwaters. Source: Hultberg and Wenblad (1980)

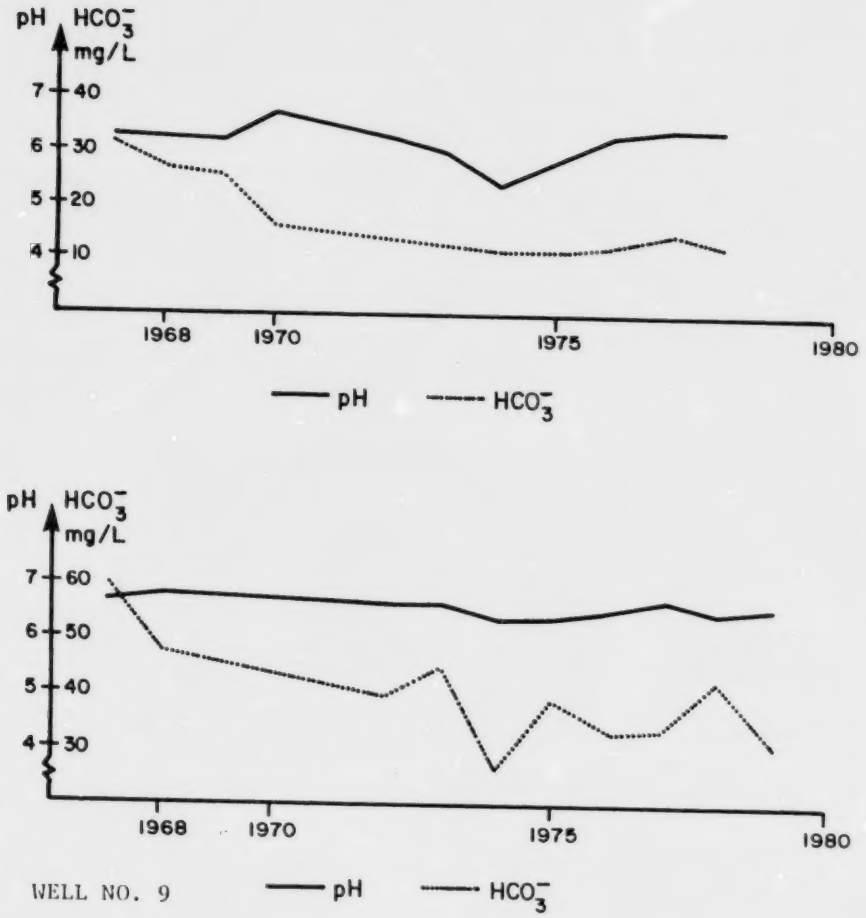

Figure 16. Bicarbonate concentrations of groundwater versus pH. Source: Hultberg and Wenblad (1980)

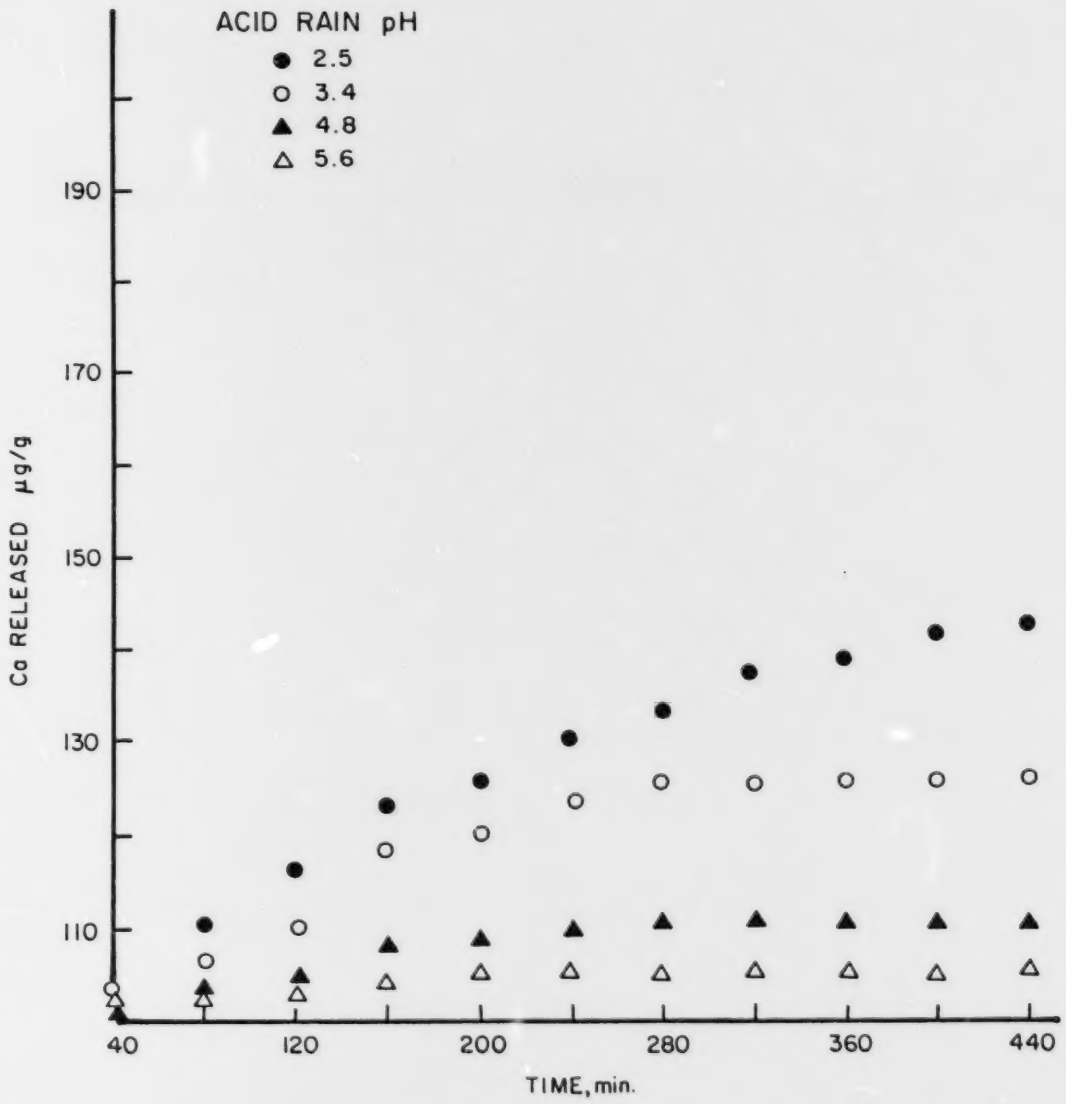

Figure 17. Calcium (Ca) release versus pH of rainwater. Source: Sparks and Curtis (1983)

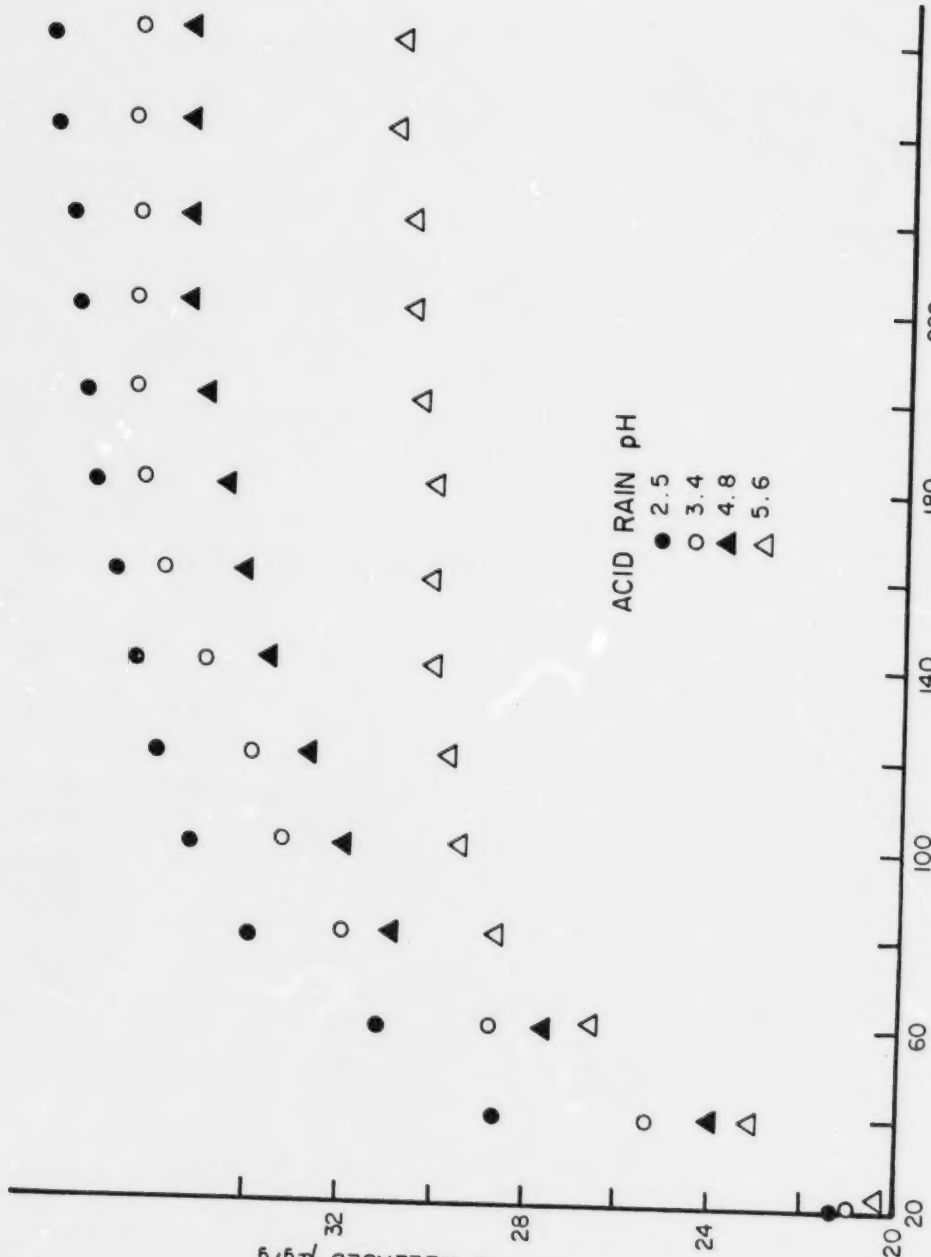

Figure 18. Potassium (K) release versus pH of rainwater. Source: Sparks and Curtis (1983)

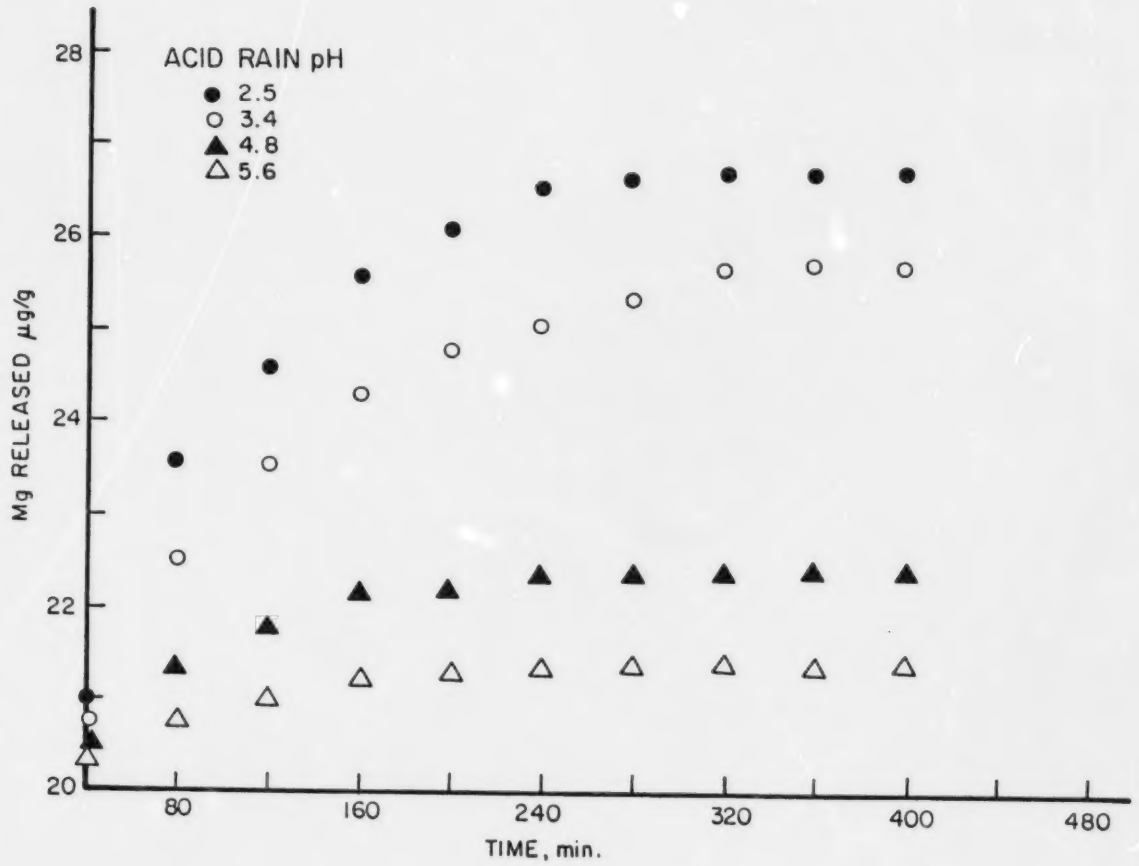

Figure 19. Magnesium (Mg) release versus pH of rainwater. Source: Sparks and Curtis (1983)

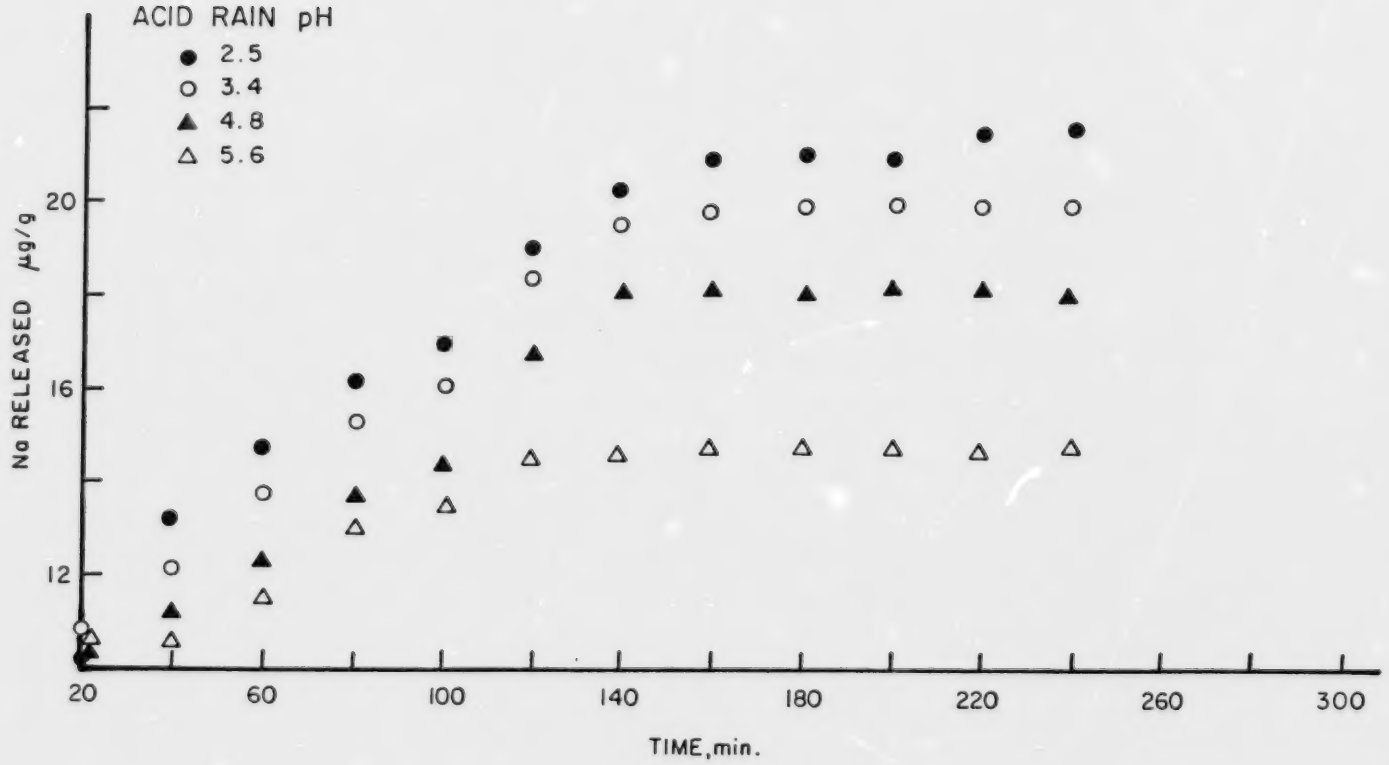

Figure 20. Sodium (Na) release versus pH of rainwater. Source: Sparks and Curtis (1983)

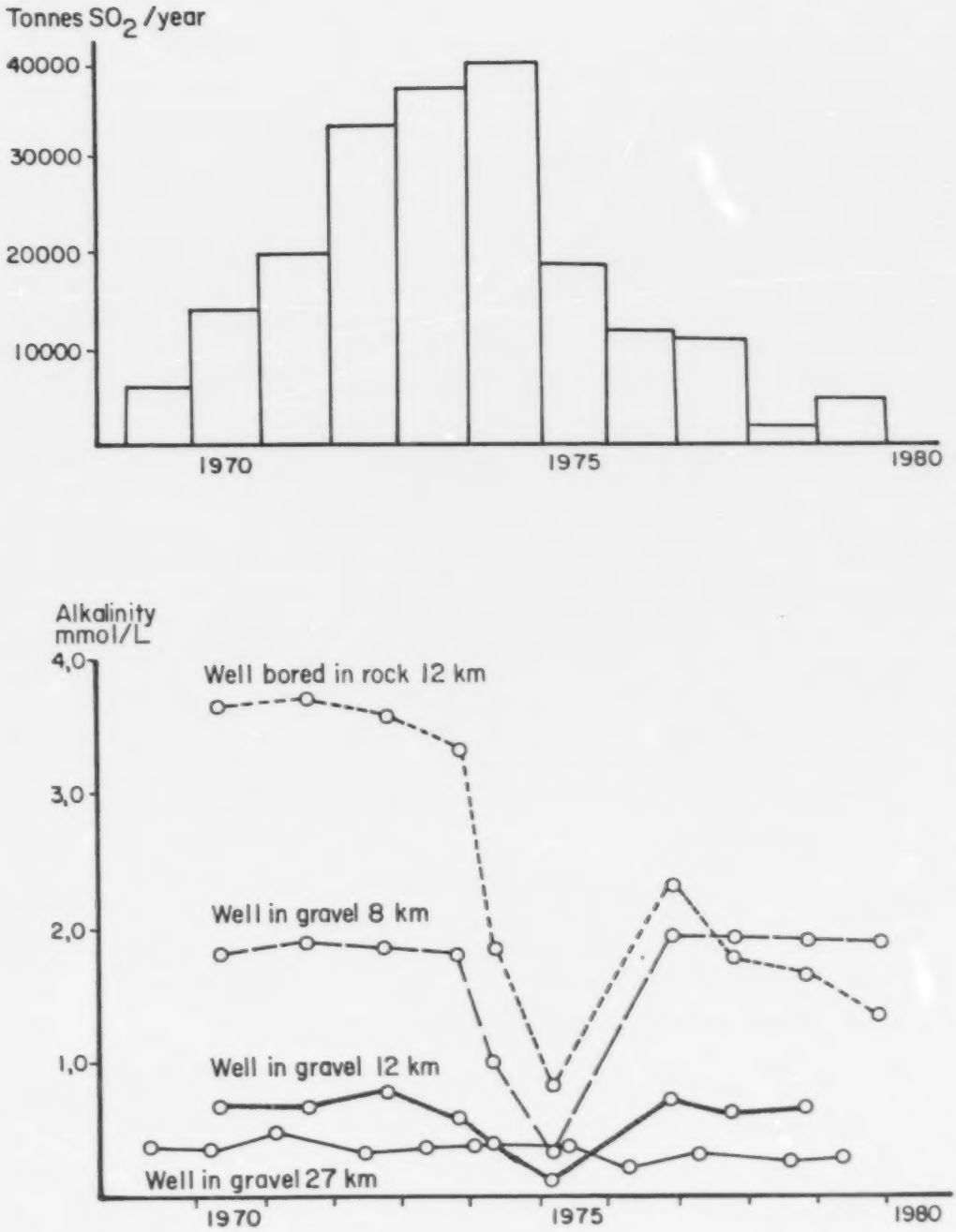

Figure 21. Sulphur dioxide emissions and alkalinity of municipal groundwater near Karlshamn, Sweden. Source: SNV (1981), in Swedish Ministry of Agriculture (1982)

increase in the calcium concentration was shown in aquifers which had decreasing alkalinity.

2.4.2.2 Sulphate. Sulphur is present in both organic and inorganic compounds in the environment. Sulphur compounds enter the aquatic environment from the weathering of rocks and soils, from atmospheric precipitation and dry fallout, and through anthropogenic inputs such as the use of fertilizers. The atmospheric sources which are greatly increased by the combustion products of industry, dominate all other sources. Figure 22 illustrates the major forms of sulphur and their inter-conversions in nature. It is apparent from this figure that sulphur is involved in a complex variety of organic and inorganic chemical processes in the subsurface. Sulphate (SO_4^{2-}) is the predominant inorganic form of sulphur, and is a stable, highly oxidized form of sulphur. The sulphate ion is readily soluble in water. Sulphate may be leached from most sedimentary rocks including shales, with the most appreciable contributions from sulphate deposits such as gypsum and anhydrite. Due to its ubiquitous presence in geological materials, sulphate is a common, dissolved constituent of groundwaters. Concentrations of sulphate in groundwater may range over four orders of magnitude. As well, sulphate concentrations in a given aquifer vary both temporally and spatially.

Investigations conducted in Sweden (Hultberg and Wenblad 1980; Martensson 1981, cited by Hultberg and Johansson 1981) suggested a relationship between atmospheric sulphate loading and the sulphate concentrations in groundwater. During the 15 years for which data are available, the shallow aquifers of less than 1.5 m depth have received approximately 1.8 tonnes of sulphate per hectare. The total sulphate deposition in the whole investigated part of the drainage area to Stenunge Stream (7.0 km^2) has been 1260 tonnes during the last 15 years. This has resulted in generally elevated concentrations of sulphates in both groundwater and surface water.

The sulphate concentration ranged from 15 to 27 µg/L in groundwater in the sandy soils surrounding the clay area in the centre of the valley. The sulphate content of the stream water upstream of the three areas with very acidic groundwater was 24-38 µg/L, which is 72 times greater than the sulphate concentration found in acid surface waters in southwestern Sweden. Downstream at the uppermost situated aquifer with very acidic groundwater, the sulphate concentration of the stream water increased to 108-210 µg/L.

In a simulation of acid rain on a quartzipsamment soil in Florida, Volk and Byers (1983) showed the movement of SO_4^{2-} during the irrigation period at two depths. Sulphate at the 15 cm depth increased rapidly from its initial concentration (Figure 23). The results indicated that SO_4^{2-} at low levels is relatively mobile in the upper 15 cm of this sandy soil. There is obviously a capacity for some initial adsorption. At the 75 cm depth, approximately 65% of the total added SO_4^{2-} at the higher concentrations (41 mg/L) was adsorbed by the soil above this depth, with lesser relative adsorption (40% and 38%) at the lower SO_4 concentrations (14 and 17 mg/L, respectively). It is not unreasonable to project that a higher percentage of the SO_4^{2-} would be adsorbed at even greater depths.

In laboratory leaching experiments conducted on three Delaware soils, Sparks and Curtis (1983) reported that during the leaching tests, the release of Cl^-, NO_3^-, and

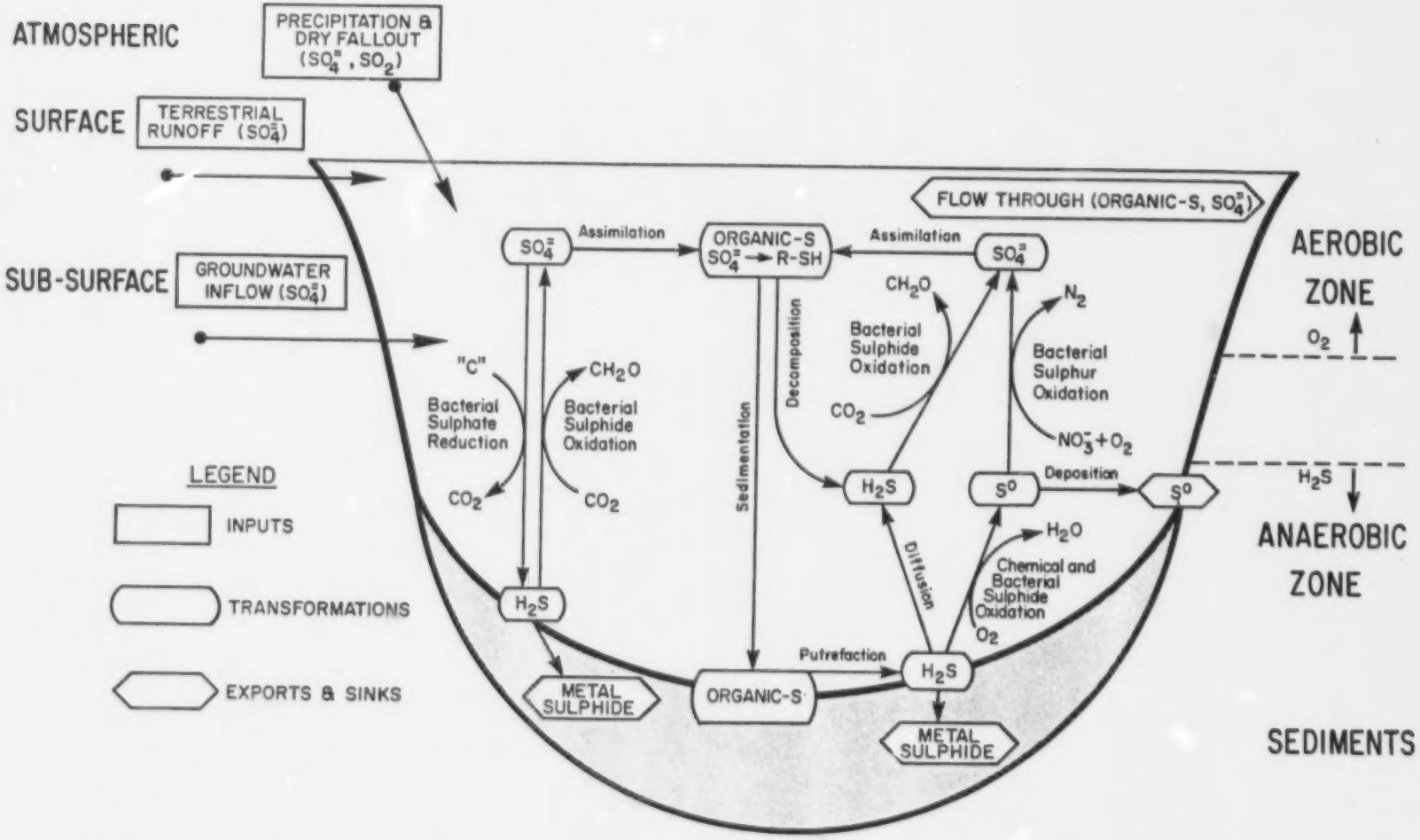

Figure 22. The sulphur cycle. Source: Wetzel (1975)

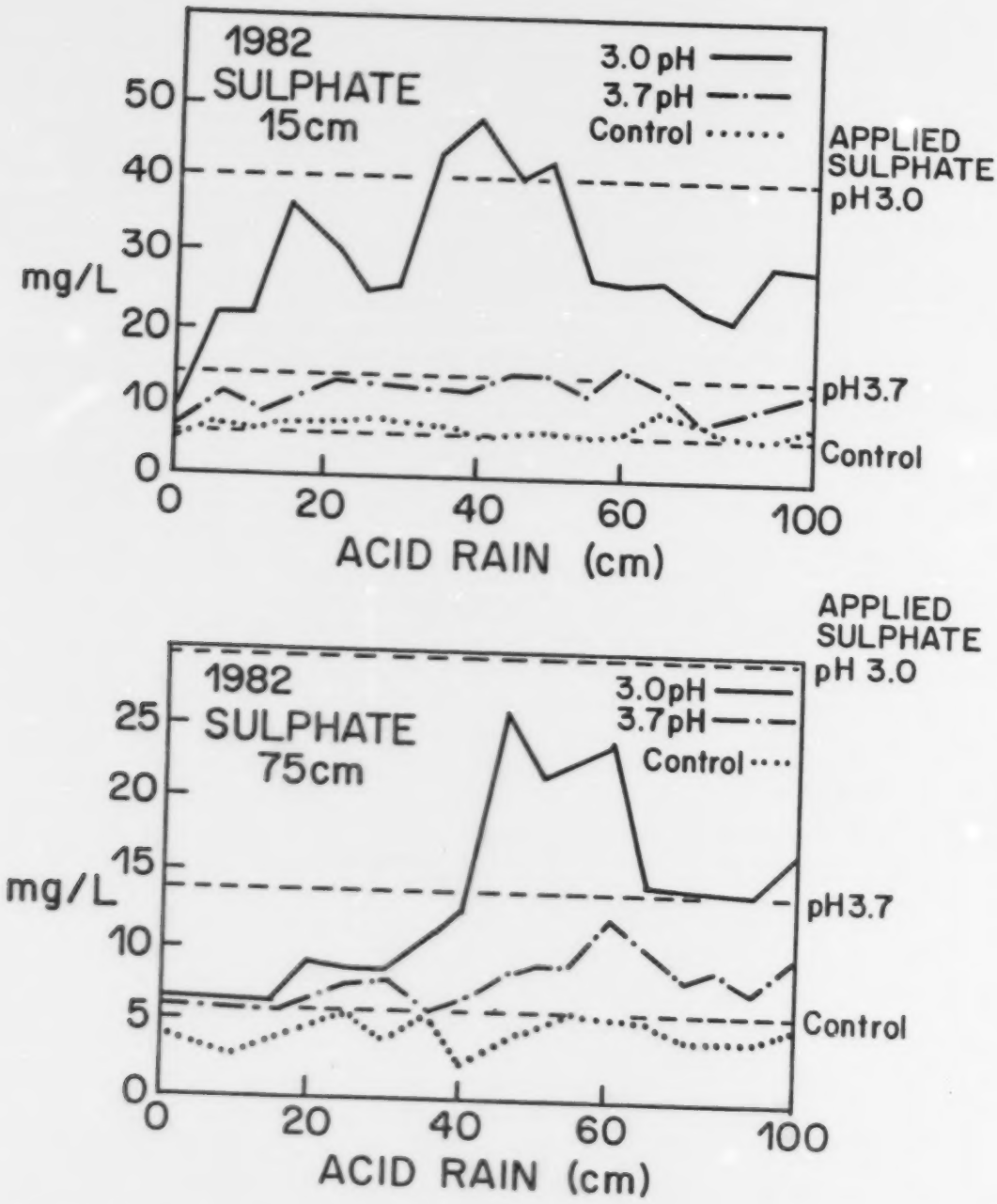

Figure 23. Effects of acid rain irrigations at pH 3.0, 3.7, and 4.7 (control) on the level of SO_4 in soil solution samplers at 15 or 75 cm soil depths under field conditions. Source: Volk and Byers (1983)

SO_4^{2-} was negligible. Lee and Weber (1982), after conducting extended in situ leaching tests, also found that for the first six months of the test no apparent differences in SO_4^{2-} concentrations were observed. Later in the experiment, increased SO_4^{2-} concentrations corresponded to decreased pH. Lee and Weber concluded that increased acidic deposition would immediately lead to increased leaching of basic cations from the soil and to decreased pH of the soil solution. However, H_2SO_4 rain might not cause significantly higher SO_4^{2-} concentrations in soil solutions until the ability of the soil to absorb SO_4^{2-} was exhausted. The results suggested that, for a strong SO_4^{2-} adsorber, this might occur after a year or two of rain at pH 4.0. The response of soil solutions to HNO_3 rain could be more rapid, but lower in magnitude. Johnson et al. (1982), in a study of numerous soil types in a variety of climatic zones, concluded that acidic deposition can cause increased leaching of base cations from soils if the associated anion (SO_4^{2-} or NO_3^-) is mobile in the soil. This is not always the case, because SO_4^{2-} can be immobilized by adsorption to Fe and Al oxides in soil.

In his discussion of the mechanisms of adsorption, Wiklander (1980) concluded that the capacity of soils to adsorb and retain anions increases with increasing pH, with the salt concentrations, and with the concentrations of hydrated oxides of Fe and Al.

Johnson and Reuss (1984) have taken the adsorption process a step further. In their discussion of how soil mediates the effects of atmospheric sulphur and nitrogen deposition, they concluded that atmospherically deposited S in excess of biological requirements often accumulates by SO_4^{2-} adsorption on to Fe and Al oxides in highly weathered soils, causing the release of OH^- which can neutralize incoming H^+, or an increase in cation exchange capacity.

When the adsorption capacity is exceeded, cation leaching is accelerated by the mobile SO_4^{2-} anions. Johnson (1979) concluded by stating that the ultimate effects of both atmospheric S and N deposition will be highly site-specific in nature, depending both on inherent site characteristics and amounts and duration of atmospheric input. Thus, benefits of S and N deposition may outweigh negative effects at some sites, whereas the reverse may be true for other sites, making broad global generalizations hazardous.

2.4.2.3 Nitrogen. Nitrogen is one of the more abundant elements, not only in the atmosphere and biosphere, but also in the outer crust of the earth and the hydrosphere. In rocks and water, however, it is far less abundant than carbon and oxygen. Mansfield and Boardman (1932) listed naturally occurring nitrate deposits in the United States in three categories: core deposits, caliche deposits, and playa deposits.

The chemical and biological processes that involve nitrogen in the shallow subsurface are relatively well understood by soil scientists. A detailed description of these processes is presented in the report on the soils component of this study (Turchenek et al. 1987). A generalized schematic diagram of the sources and pathways of nitrogen in the subsurface environment is shown in Figure 24 to indicate the complexity of the processes.

The wide distribution of nitroger compounds in natural waters and their role in life processes make their study of immediate importance as a contribution to an understanding of the geochemistry of water. Nitrogen compounds in water may be deleterious to health, injurious in industrial processes, and either ultra-injurious or beneficial in agriculture.

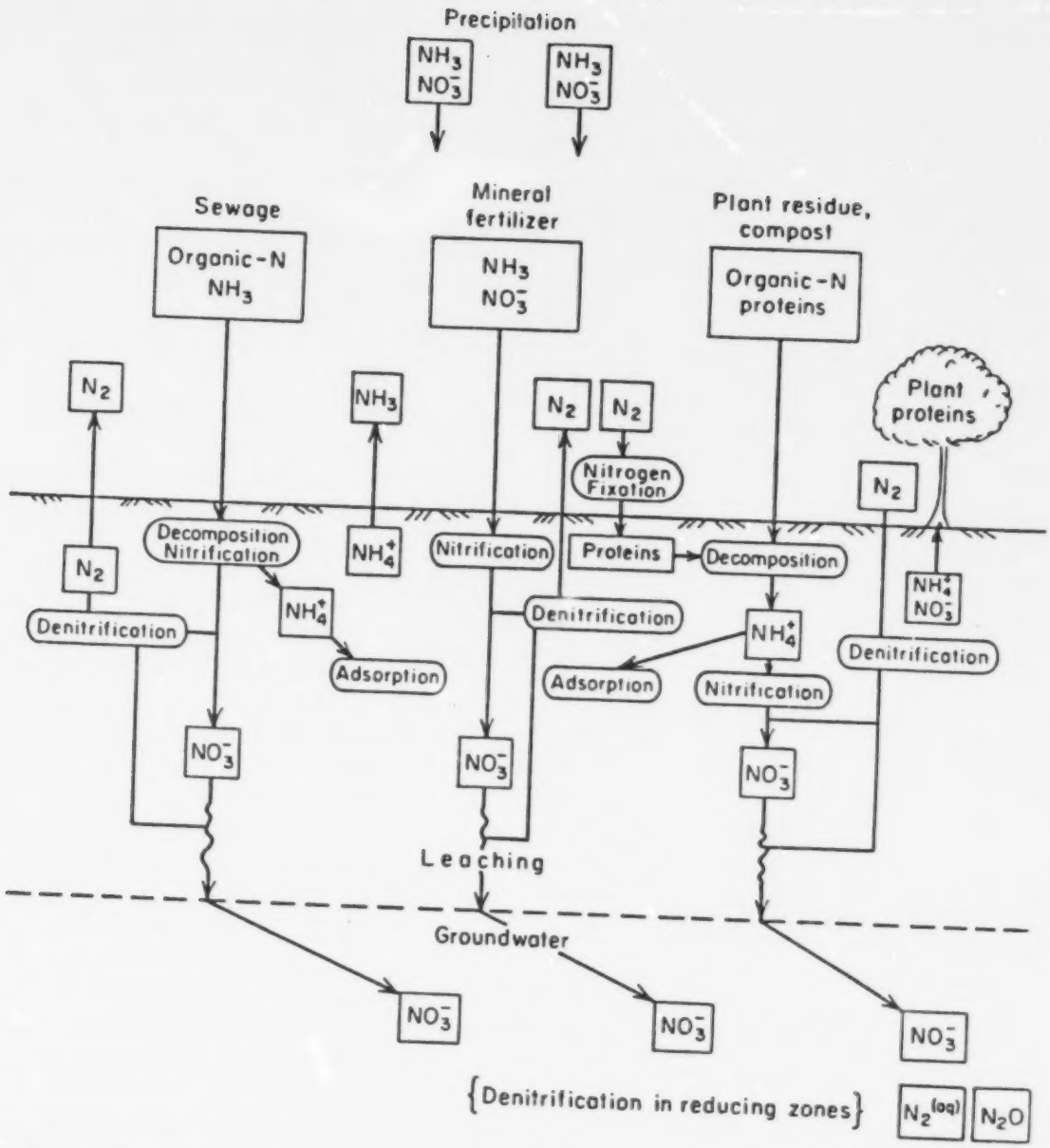

Figure 24. Sources and pathways of nitrogen in the subsurface environment. Source: Freeze and Cherry (1979)

Substantial increases in nitrogen compounds in a surface water or groundwater system, progressively with time or at a single time, may reflect pollution from such sources as domestic and barnyard wastes or return flow from irrigation.

Much of the following discussion is in terms of NO_3^- (nitrate) for two reasons: (1) NO_3^- is the end member of the oxidation chain of nitrogen in water and the form in which, presumably, it occurs most abundantly and commonly, especially in groundwater; and (2) it is the nitrogen-bearing ion most commonly analysed for and reported in the literature in the United States. Exceptions occur in studies oriented to public health and in some soil studies. Because NO_2^- (nitrite) and NH_4^+ (ammonium ion) are generally transitory, the analytical statement may not represent the form in which nitrogen compounds actually occur in situ.

Nitrate concentrations in surface waters range from below the limit of detection to more than 100 ppm. In groundwater the range is from below the limit of detection to more than 1000 ppm. Rainwater and Thatcher (1960) stated that unpolluted water seldom contains more than 10 ppm (as N) of nitrogen compounds. George and Hastings (1951), working in Texas, cited 5 to 10 ppm NO_3^- as a common upper limit and in their study considered water with more than 20 ppm NO_3^- to be abnormal.

More than 950 analyses of groundwater have shown that two-thirds of the reported NO_3^- concentrations fall in the range of less than 0.1 to 9.0 ppm (Feth (1966). The analyses examined are of water from diverse geological sources across the United States that had dissolved solids concentrations ranging from less than 100 mg/L to more than 100,000 mg/L.

By and large, few wells or springs are sampled repeatedly except those wells used for monitoring chemical quality changes. Limited data presented by Feth (1966) showed temporal variations in nitrate concentrations of up to 31 ppm. Rainwater and Thatcher (1960) reported that the absence of a correlation between the NO_3^- and Cl^- content of groundwater indicates that the nitrogen does not reflect sewage pollution.

Seasonal variations in NO_3^- concentrations of as much as 15 ppm were reported by Metzler and Stoltenberg (1950) from municipal wells in Kansas. The authors inferred that seasonal leaching of nitrogen from the soil was responsible for the variations observed. Similar summer-winter variations have been reported by others (Piper et al. 1953; and Feth et al. 1964).

The study of nitrogen compounds in groundwater is complicated by the many sources from which the compounds are derived and by the intimate involvement of nitrogen with life processes.

Fertilizers are added to croplands in part to increase the amount of nitrogen available to the plants. The nitrogen used is largely in forms such as ammonium sulphate, anhydrous ammonia, ammonium nitrate, sodium nitrate, calcium nitrate, and various ammoniated phsophates and super phosphates. These forms are typically highly soluble. Where precipitation or irrigation is periodically in excess of plant requirements, downward-percolating water doubtless carries with it nitrogen compounds from fertilizers.

Allison (1955), in attempting to provide a nitrogen balance sheet for harvested lands in the United States, indicated that an average of approximately 27 kg of nitrogen are leached per hectare per year. This is a potential source of nitrogen in surface water and groundwater. This amount, if added to groundwater, would explain the fairly high concentrations of NO_3^- in some areas.

Barnyard and silo effluents undoubtedly are important sources for nitrogen in water. Deutsch (1963) reported nitrate concentrations of 243-975 ppm in water from shallow dug wells in several counties in Michigan. The investigation was occasioned by several cases of infant methomoglobinemia which, in susceptible infants, may occur if water containing more than about 10 ppm NO_3^--N is ingested (McKee and Wolf 1963, cited by McNeely et al. 1979). Waste from feedlot operations also adds to the nitrogen load of water (Feth 1966). Feedlot feeds are selected, in part, for their high nitrogen content to stimulate protein synthesis in the animals.

Garbage, sewage, and industrial wastes, especially the latter two, are well known sources of nitrogen compounds in water. The normal range of mineral pick-up in domestic sewage is shown in Table 4. The concentrations cited in the table are, of course, additive to those already present in the domestic water supply. The contributions of nitrogen from sanitary fills are less well known, although one study (California State Water Pollution Control Board 1961) reported 1300 ppm of ammonia and organic nitrogen in percolate from refuse.

The ultimate fate of nitrates that enter the groundwater system is poorly understood. Intuitively, one can assume that if no adsorption mechanisms for nitrate are active below the water table, the nitrates that enter the groundwater regime will be carried to a point of discharge. Chen et al. (1972) have documented a denitrification of groundwaters that seep through lake bottom sediments.

While the alteration of nitrate below the water table is generally considered to be limited, Correll et al. (1984) reported that, although in a cropland little seasonal variation in nitrate concentrations was observed, groundwater leaving the cultivated portions of cropland each season contained high calcium, magnesium sulphate, and nitrate concentrations. After traversing 50-100 metres of riparian forest, nitrate, magnesium, and calcium concentrations were reduced by 94%, 33%, and 37%, respectively.

In England, dramatic increases in SO_4^{2-} and NO_3^- levels have been observed in groundwater in East Yorkshire (Foster et al. 1982). Intensive analysis of this groundwater chemistry led the authors to conclude that changes in farming practices and the application of various forms of nitrogen fertilizers are contributing factors.

Atmospheric N additions in most regions make only a minor contribution to agricultural production. Crop N requirements are high (100-300 kg ha^{-1} y^{-1}), and routine fertilization rates usually greatly exceed atmospheric inputs. When the supply of nitrogen exceeds the demand in well drained systems, nitrogen output will largely be in the form of NO_3^- leaching.

Many forests are N deficient, however, and atmospheric-derived N is usually rapidly immobilized by ecosystem biota. This retention precludes NO_3^- losses causing cation leaching and may even result in increased forest growth (Abrahamsen 1980). However, exceptions occur when N supplies are excessively enriched, whether by natural processes (for example, N fixation), fertilization, or by atmospheric inputs.

Van Miegroet and Cole (1984, cited by Johnson and Reuss 1984) recorded high rates of NO_3^- and associated leaching in soils beneath red alder, an N-fixing species. Tamm and Popovic (1974, cited by Johnson and Reuss 1984) and van Breeman et al. (1982) have documented increased soil acidification and leaching associated with repeated fertilization with nitrogen.

Table 4. Normal range of mineral pick-up in domestic sewage (from California Department of Water Resources 1961, in Feth 1966).

Mineral	Normal Range (ppm)
Dissolved solids	100-300
Boron (B)	0.1-0.4
Sodium (Na)	40-70
Potassium (K)	7-15
Magnesium (Mg)	3-6
Calcium (Ca)	6-16
Total nitrogen (N)	20-40
Phosphate (PO_4)	20-40
Sulphate (SO_4)	15-30
Chloride (Cl)	20-50
Alkalinity (as $CaCO_2$)	100-150

When a nitrogen-deficient ecosystem is impacted, a very simple conceptual model of the acidification effects of nitrogen can be involved. The first effect is an increased rate of biomass production and an increase in the rate of uptake of basic cations from the soil. The cation uptake is in itself acidifying. If the input rates are moderate, most of the increased nitrogen input will be tied up in the increased biomass, and leaching of basic cations in association with NO_3^- will be small. If the biomass is harvested, acidification will largely result from the increase in base cation removal by harvest. Further acidification may also result from cation demands of the regenerating forest. If the biomass is not harvested, the ecosystem will ultimately come to a new equilibrium. In the latter stage, the capital of both nitrogen and bases tied up in the biomass and litter components will have increased from pre-impact levels along with an increase in annual cycling rates. Nitrogen output will now increase perhaps up to the level of input, and in well drained systems this output will largely be in the form of NO_3^- leaching. Acidification will then occur to the extent that basic cations are leached in association with this NO_3^-.

NO_3^- is frequently immobilized by biological demand for N. If NO_3^- is present in excess of plant or microbial demand, leaching will occur because NO_3^- is only poorly adsorbed to soils. In any event, cation leaching caused by acidic deposition must be viewed as an increment to the natural leaching caused by internally generated carbonic, organic, and nitric acids.

Atmospheric nitrogen inputs are small relative to crop N requirements but may benefit the many N-deficient forests of North America and Scandinavia. Excessive N inputs or N inputs to N-rich forests result in net nitrification and, in some cases, increased leaching of NO_3^-.

Johnson and Reuss (1984) concluded that atmospherically deposited N seldom exceeds biological requirements. When it does, NO_3^- is rapidly leached because no adsorption reactions similar to those of sulphate exist.

Although a fraction of the groundwater and dissolved salts in natural circulation may be discharged in the year that they originated as infiltration from agricultural soils, it must be stressed that groundwater residence time often exceeds 10 or even 20 years. At considerable depth below the groundwater table, and in the deeper confined aquifers, circulation may be exceedingly slow and, in certain areas, groundwater has been dated back to at least 10,000 years. Thus, groundwater systems are quite different from surface water courses in that the effects of pollution incidents become apparent much more slowly in the water supplies but persist much longer.

2.5 METALS AND TRACE ELEMENTS

2.5.1 Aluminum

Aluminum is the third most abundant element in the earth's crust, making up 8.13% by weight. Minerals containing aluminum are common to igneous, metamorphic, and sedimentary rock types. It is not unexpected, therefore, that aluminum becomes involved in chemical weathering and geochemical reactions and subsequently becomes a component of all soil types. In spite of its relative abundance, aluminum is generally present in groundwater in concentrations usually less than 0.1 mg/L (Davis and De Wiest 1966)

although acidic waters may contain higher concentrations. Stumm and Morgan (1970) compiled data on Al levels in terrestrial waters, reporting a median Al concentration of approximately 10-20 $\mu g\ L^{-1}$. Aluminum has not been shown to be harmful to human health and, therefore, no drinking water guidelines for Al levels have been formulated. Correspondingly, routine potability testing of water supplies does not include aluminum as a parameter. As a result, limited data are available to assess temporal or geographic fluctuations in aluminum concentrations in groundwater.

Chemical alterations in the subsurface result in the release of aluminum as well as other heavy metals (Cronan et al. 1978; Babich et al. 1980; Driscoll et al. 1980; and Wainwright 1980). Volk and Byers (1983), Sparks and Curtis (1983), and Budd et al. (1981) have observed increased aluminum in soil leachate as the pH of acid rain decreased (Figures 25, 26, and 27).

The relationship between acidic storm runoff and aluminum concentrations has been observed by Sharpe et al. (1984). In this study in the Laurel Hills of southwestern Pennsylvania, aluminum concentrations were observed to rise dramatically during high runoff events (Figure 28). These increases in aluminum concentrations in streams were found to correspond to decreases in pH (Figure 29). The levels of aluminum observed were considered lethal to fish and subsequent fish surveys confirmed that no viable fish populations were present in the streams with toxic levels of dissolved aluminum.

One of the intriguing processes that has been observed in the Adirondack spodosols is the aluminum mobilization and leaching accompanying acid rainfall percolation through the soil profile. The solution acidity, DOC, and organically complexed aluminum all peak in concentration in the upper soil profile. Presumably, the concentrations of anthropogenic strong acids also peak at this depth. In contrast, the lower B horizon solutions exhibited a higher pH, a much lower DOC, lower concentrations of organically complexed aluminum, but an absolute increase in total dissolved monomeric aluminum. This pattern is interpreted to indicate that the transport of aluminum by soil-derived organic acids is primarily limited to the upper soil profile, whereas the leaching of free inorganic aluminum by precipitation, borne by strong acids, may persist through the soil profile and even into streams. The pattern also suggests that the B2 horizon has a relatively larger reservoir of labile aluminum than the O or A horizons. In general, this interaction between acid precipitation and the B horizon aluminum reservoir may be very important both in terms of soluble aluminum release and pH buffering by hydroxy-aluminum species.

Studies of the groundwater flow and quality around Lakes Bredvatten and Lysevatten in Sweden have shown that the increased concentrations of aluminum in acidic lake water are caused by acidic groundwater (Hultberg and Johansson 1981). These increased aluminum concentrations were later shown to be a major factor in the widespread ecosystem changes occurring in the lakes and water systems.

When a similar but even more pronounced soil and groundwater acidification occurred via oxidation of accumulated sulphur to sulphuric acid, thereby releasing several soil minerals to the groundwater, a number of regional investigations were carried out on wells and groundwater systems in different provinces in southern Sweden.

A study by Johansson and Hultberg (1977, cited by Hultberg and Johansson 1981) showed that inflow of acidic groundwater with elevated concentrations of metals

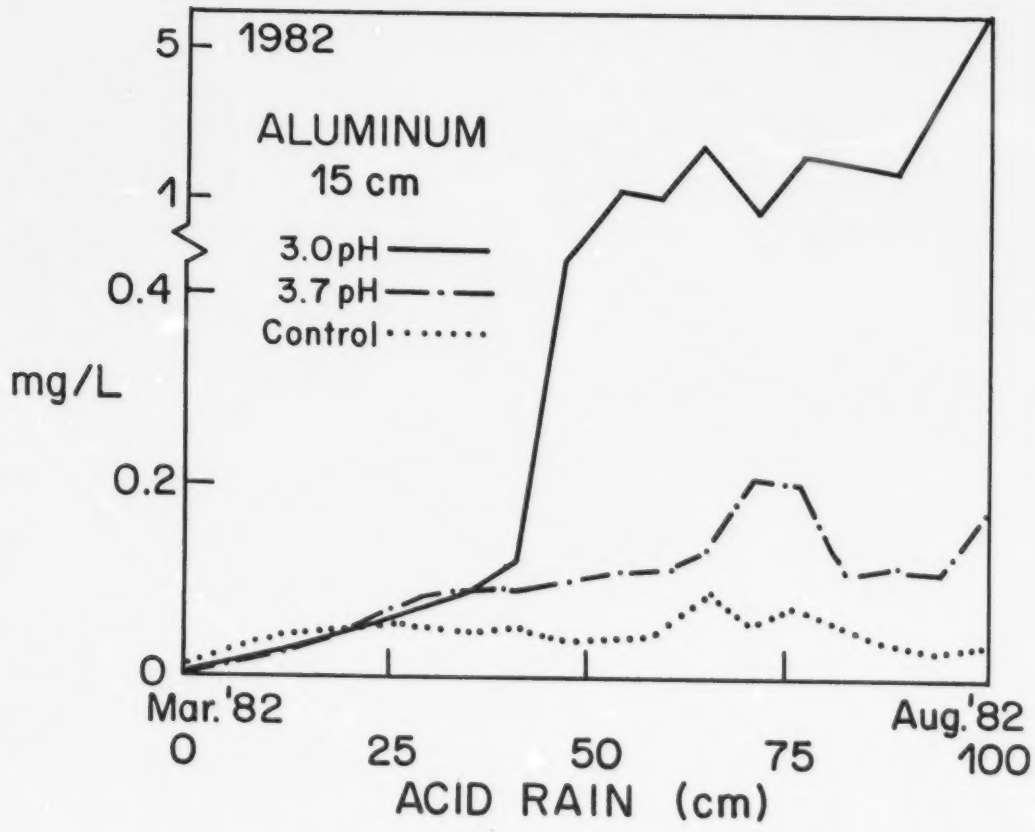

Figure 25. Effects of acid rain irrigations at pH 3.0, 3.7, or 4.7 (control) on the level of Al in soil solution samplers at 15 cm soil depths under field conditions. Source: Volk and Byers (1983)

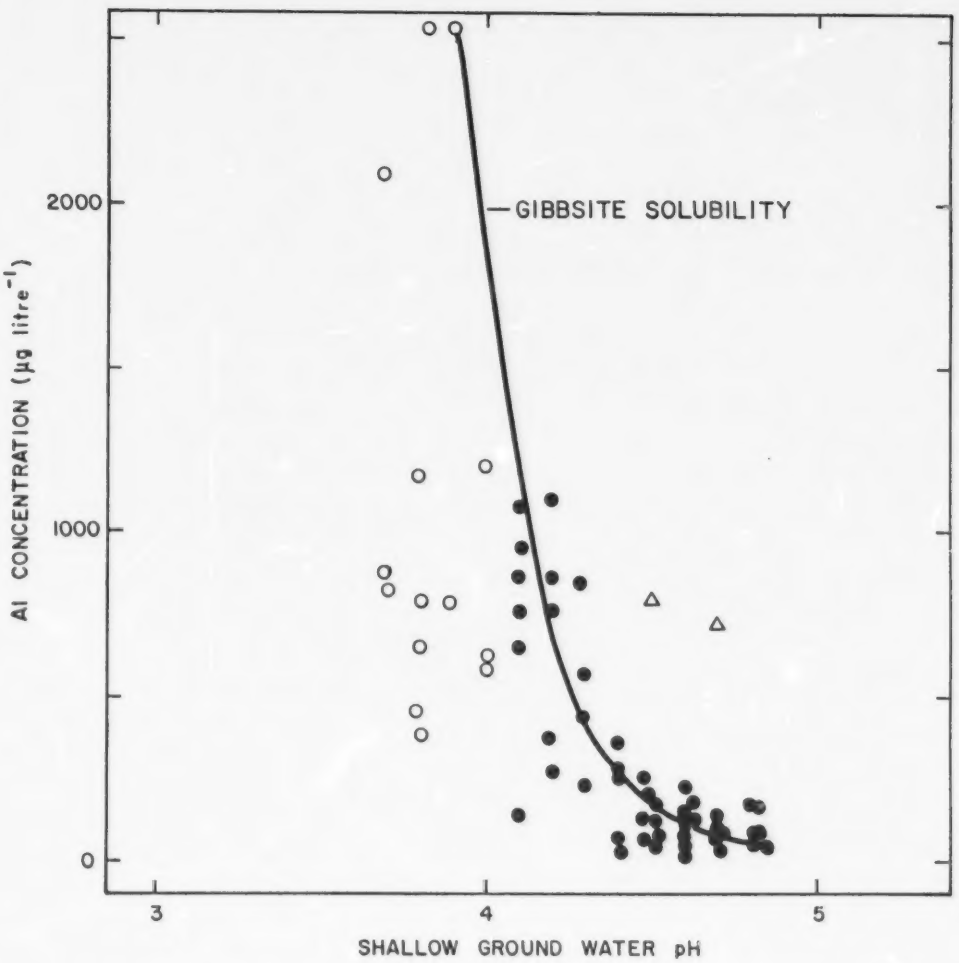

Figure 26. Groundwater Al concentration versus groundwater pH. Source: Budd et al. (1981)

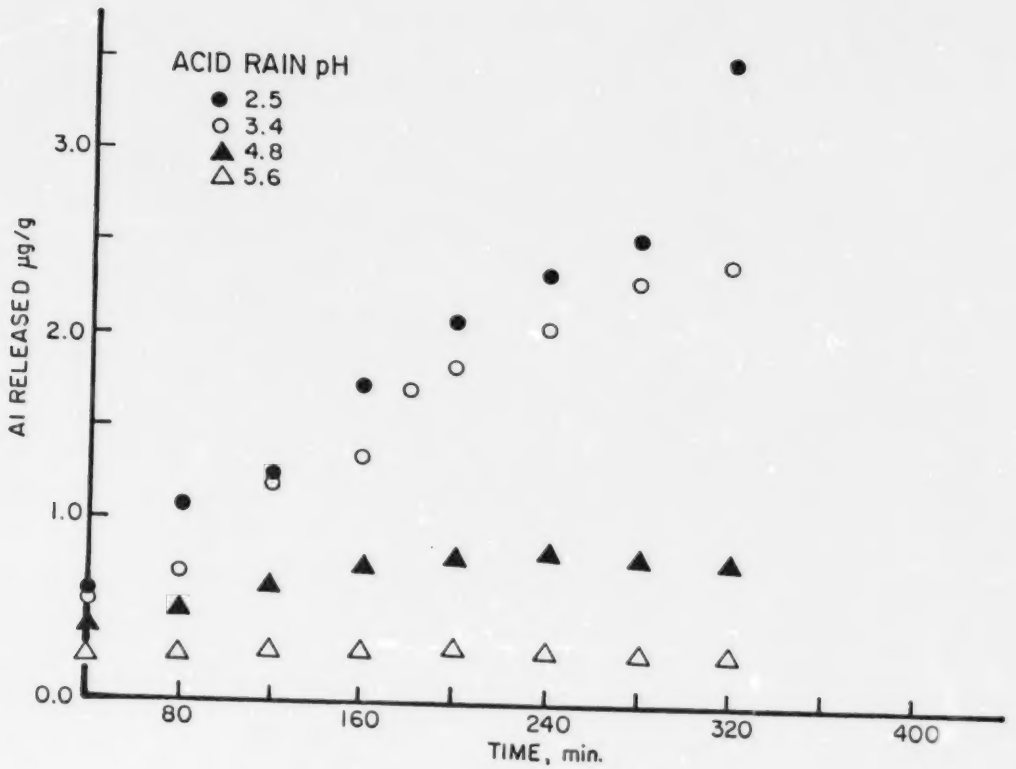

Figure 27. Aluminum release versus pH of rainwater. Source: Sparks and Curtis (1983)

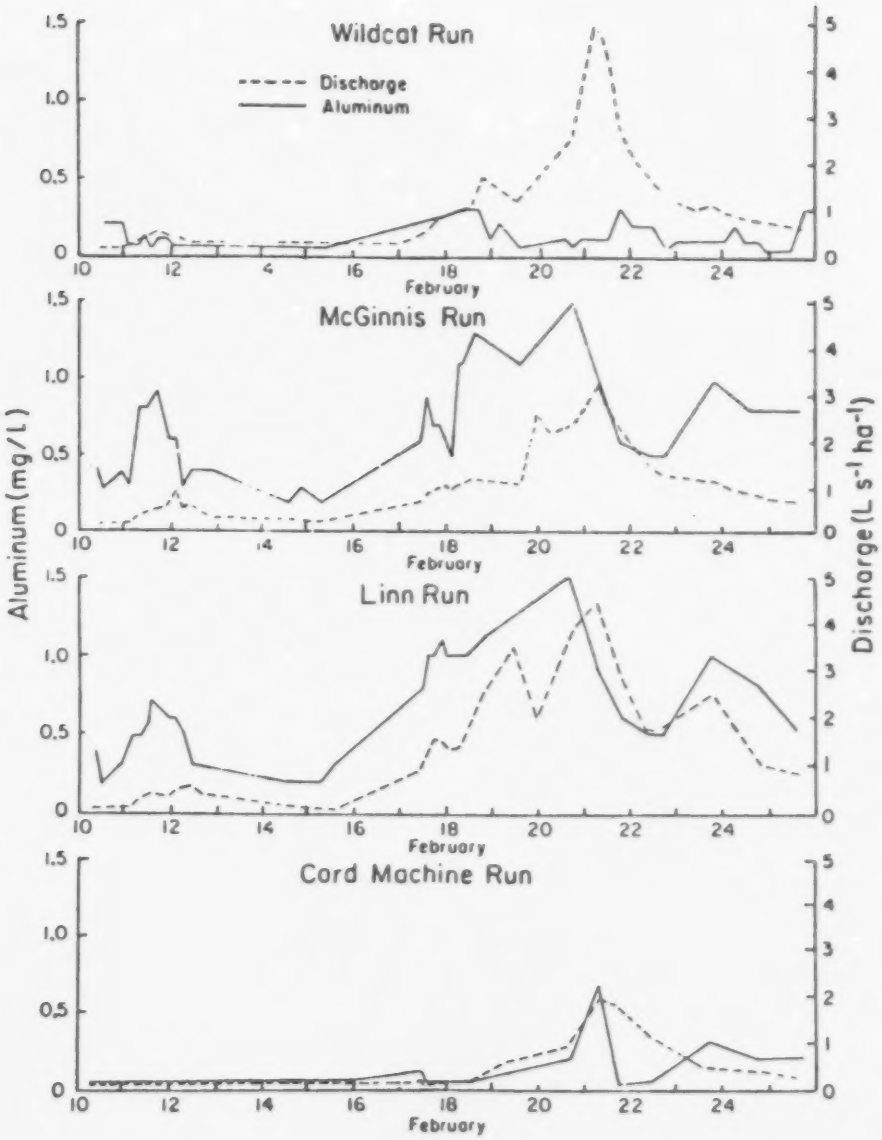

Figure 28. Comparison of discharge and total Al concentrations in four Laurel Hill streams during a major dormant season runoff event, 1981. Source: Sharpe et al. (1984)

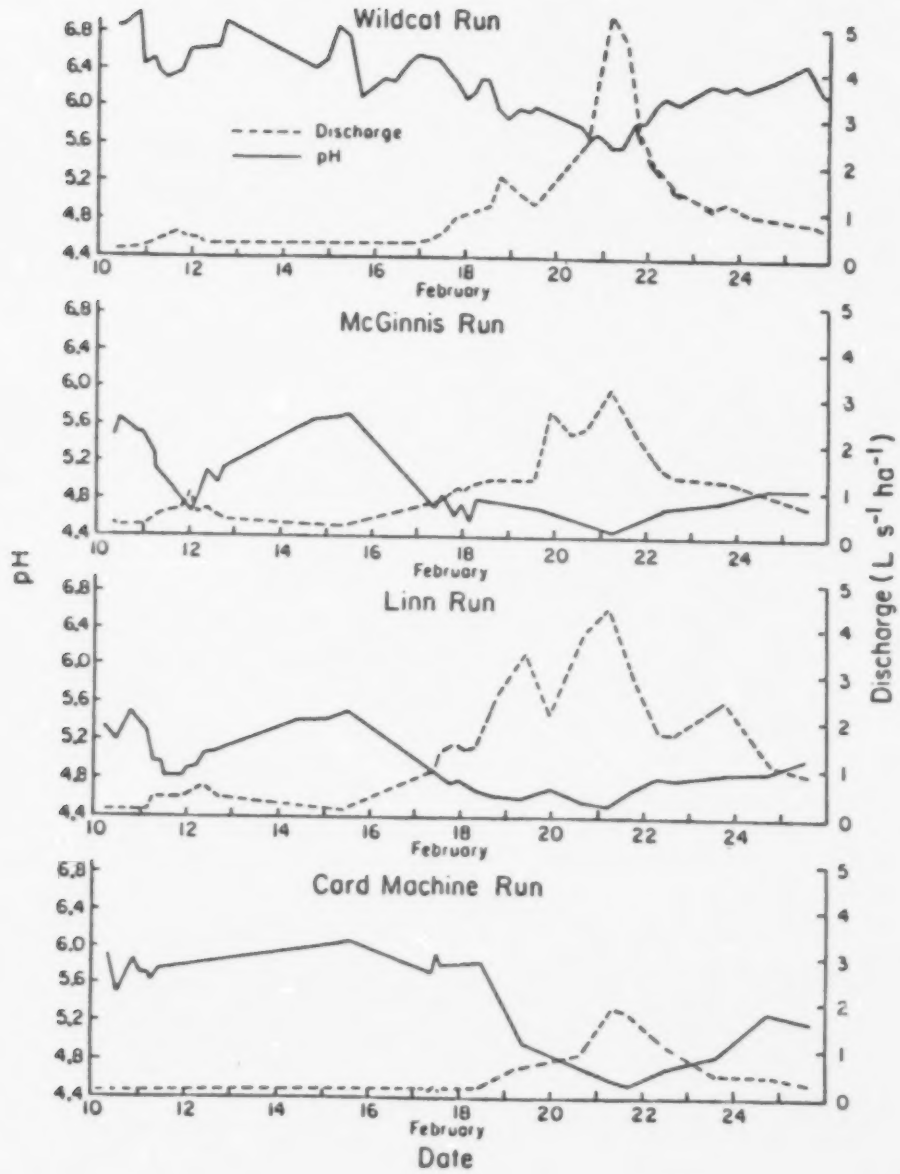

Figure 29. Comparison of stream pH and discharge on four Laurel Hill basins during a major dormant season runoff event, 1981. Source: Sharpe et al. (1984)

(including Al) was one cause of the re-acidification of limed lakes in Sweden. As well, in 1977, metal precipitates (Al, Mn, Fe, and so forth) on the bottom of a stream were shown to be caused by acid groundwater (Hultberg and Johansson 1978). As a result of these studies, the authors initiated regional surveys of the water quality in shallow and drilled private wells during 1978-1980 (Figure 30).

Sampling was performed from 1977 onwards and data to May 1979 are presented in Table 5. Stations with groundwater inflow from bog and fen areas around Bredvatten (B1, B2, B3, and B5) all had pH values below or slightly higher than 4.0 during 1977-1979. This soil type represents a groundwater inflow of 56% of the drainage area of the lake. The groundwater from moraines at Station B4 had a somewhat higher pH (4.3-4.6) and a higher concentration of aluminum (2.6-1.9 mg/L) and manganese (0.3-0.2 mg/L). The aluminum concentrations were, however, high in all sampled areas and this partly explained the decreased pH and alkalinity in the lake water which appeared at high groundwater inflow to Bredvatten in 1977. The acidic groundwater with increased levels of aluminum and manganese indicated that a long-term acidification of the soils had occurred in the drainage area of the lake.

The elevated concentrations also indicated that the store of aluminum in the podzol profile had decreased and that a generally increased mobility was caused by the low pH in the soil water. The high aluminum concentrations also showed that the moraine around Lake Bredvatten is thinner than the glaciofluvial deposits at Lysevatten, where aluminum is still retained in the soil profile. The groundwater around Lake Lysevatten has a generally higher pH than around Lake Bredvatten and the re-acidification also is slower compared to Lake Bredvatten (Table 6).

The amount of inflow from bog and fen areas to Lake Lysevatten was one half (27%) of that to Lake Bredvatten (56%) and there the pH was 4.17-4.36 compared to <4.0 at Bredvatten. The inflow from the moraines (L2, L3) was less acidic and pH was 4.29-4.84; however, as in the moraine at Bredvatten, there were high aluminum concentrations (1.3-0.74 mg/L). The groundwater inflow from glaciofluvin has higher pH values (5.2-5.95) and low concentrations of aluminum (Figure 31).

The investigated part of the drainage area to Stenunge Stream is a small farmed valley at 85-95 m above sea level surrounded by a bedrock ridge of gneiss with a maximum elevation of 115-135 m above sea level, with softwoods on a thin soil cover (Hultberg and Johansson 1981). In the valley, the soil within a boundary along the bedrock ridge and the centre of the valley is sand or sandy silt which covers (with a 1.2 m thick layer) the top of the moraine clay in the centre of the valley. Groundwater and soil samples were collected after drilling both in the sandy areas surrounding the central clay areas and underneath the clay in a sandy/gravelly layer onto the bedrock, as well as in dug pits in the shallow aquifer on top of the clay. Groundwater pH from the sandy area (data from three drilled holes) varied between 5.1-5.7 at depths of 5.0-8.5 metres in April, 1978 and increased to 5.8-6.2 in May, 1978.

Groundwater pH from the aquifers underneath the clay layer was 7.0 and the alkalinity (0.54 mg/L) and tritium analyses showed that this water was 20 years old compared to water <2 years in the shallow aquifer on top of the clay where pH was very low (3.2-4.8) and where there were high concentrations of aluminum, manganese, and so forth.

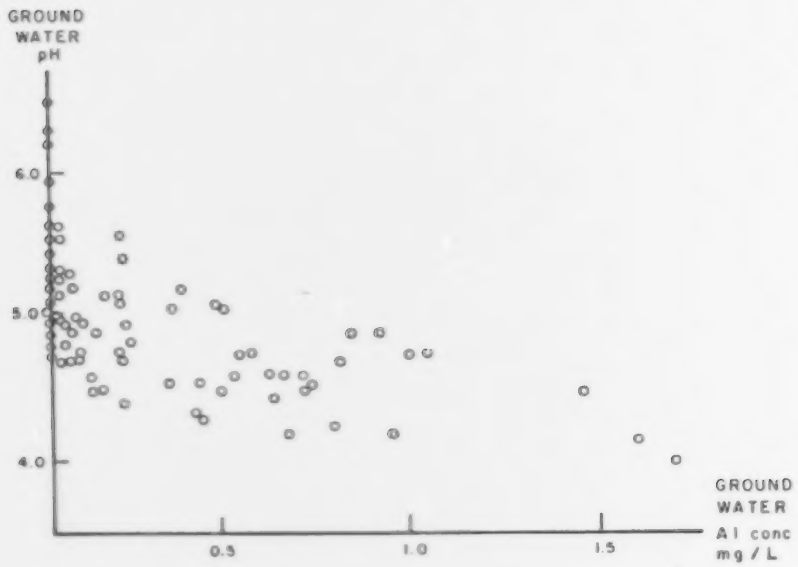

Figure 30. Aluminum concentration in shallow wells in the Province of Bohuslan, Sweden. Source: Hultberg and Wenblad (1980)

Table 5. Lake Bredvatten quality of inflowing groundwater. (Source: Hultberg and Johansson 1981)

		pH	Colour (mg Pt/L)	H_2 (mS/m)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	SO_4^{2-} (mg/L)	Cl (mg/L)	Tot-P[1] (mg/L)	Solved Al (mg/L)	Solved Mn (mg/L)	Solved Fe (mg/L)
B 1	771012	3.90	58	12.5	1.7	1.6	16	-	-	0.6	0.03	0.37
	780428	4.17	138	8.3	2.8	-	9.1	5.7	0.008	0.36	<0.03	0.37
	780815	3.93	85	12.9	2.5	-	12	-	0.014	0.98	0.005	0.23
	781010	3.87	102	12.5	1.9	-	17.4	9.0	+	0.13	0.005	0.15
	790510	3.94	33	12.2	1.8	-	15.3	-	0.002	0.71	0.033	0.12
B 2	771012	3.85	55	12.6	2.0	1.8	20	-	-	0.5	0.03	0.09
	780428	3.89	26	10.6	1.9	-	14.4	5.7	0.017	0.88	0.03	<0.05
	780815	4.00	93	13.0	2.5	-	12	-	0.003	0.38	0.05	0.92
	781010	3.93	212	10.4	1.7	-	10.1	9.4	-	0.66	0.036	0.83
	790510	3.88	102	12.8	1.6	-	14.3	-	0.009	0.39	0.036	0.57
B 3	771012	3.85	106	14.3	2.4	2.5	12	-	-	1.0	0.04	0.56
	780428	3.86	55	11.4	1.4	-	14.4	7.8	0.011	0.66	<0.03	0.28
	780815	4.53	50	13.4	4.3	-	30.4	-	0.015	0.80	0.095	0.43
	781010	3.84	137	14.0	1.9	-	16.9	14.5	-	0.12	0.031	0.73
	790510	3.91	66	13.6	1.6	-	15.3	-	0.006	0.76	0.044	0.71
B 4	771012	4.30	14	15.6	2.6	2.4	26	-	-	2.6	0.25	<0.03
	780428	4.65	1	10.3	1.9	-	24	7.8	0.024	1.9	0.20	<0.05
	780815	----------										Dry
	781010	4.54	10.5	13.1	2.2	-	30.2	17.5	-	2.0	0.24	<0.05
	790510		3	13.3	2.3	-	25.5	-	0.003	2.3	0.20	0.28
B 5	771012	3.88	425	11.4	2.6	1.6	9	-	-	1.0	0.05	0.97
	780428	4.37	207	5.0	2.2	-	28	3.9	0.032	0.6	<0.03	0.39
	780815	4.23	251	7.3	2.2	-	4.6	-	0.012	0.92	0.29	0.54
	781010	4.19	313	6.7	1.8	-	1.6	6.6	+	0.88	0.033	0.88
	790510	4.16	301	7.2	1.3	-	4.2	-		0.91	0.12	0.80

[1] No explanation for '+' given in original table.

Table 6. Lake Lysevatten quality of inflowing groundwater. (Source: Hultberg and Johansson 1981)

		pH	Colour (mg Pt/L)	H_2 (mS/m)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	SO_4^{2-} (mg/L)	Cl (mg/L)	Tot-P[1] (mg/L)	Solved Al (mg/L)	Solved Mn (mg/L)	Solved Fe (mg/L)	Alkalinity (mekv/L)
L 1	771012	5.30	20	18.0	6.2	4.0	30.0	-	-	0.1	0.03	0.09	0
	780428	5.96	7	13.3	6.4	-	13.4	-	0.018	0.23	<0.03	<0.05	0.042
	780821	----------											
	781013	----------											Dry
	790515	5.72	11	13.1	4.6	-	16.4	-	0.019	0.47	0.009	0.45	Dry
L 2	771012	4.55	15	8.8	2.2	1.2	12.0	-	-	1.2	0.11	<0.03	0.032
	780428	4.72	6	5.2	1.4	-	9.1	2.8	0.017	1.1	0.05	<0.05	0
	780821	4.84	16	7.0	4.0	-	12.8	-	0.015	0.9	0.08	0.04	0
	781013	4.29	46	8.3	2.5	-	12.1	8.7	+	0.74	0.04	0.15	0
	790515	4.48	20	7.7	2.2	-	11.7	-	0.007	1.0	0.076	0.58	0
L 3	771012	4.35	39	8.9	2.6	1.3	12.0	-	-	0.9	0.10	0.33	0
	780428	4.48	16	6.6	2.0	-	10.6	4.3	0.015	0.8	0.05	0.10	0
	780821	4.95	5.3	5.5	1.8	-	12.0	-	0.001	0.96	0.08	0.03	0
	781013	4.75	28	7.3	1.8	-	10.1	7.9	+	1.1	0.10	0.05	0
	790515	4.80	3	5.6	1.4	-	11.2	-	0.004	1.3	0.095	0.18	0
L 4	771012	4.22	100	9.2	2.4	1.4	12.0	-	-	0.4	0.03	0.39	0
	780428	4.17	137	7.2	2.0	-	7.0	5.3	0.018	0.27	<0.03	0.24	0
	780821	4.36	53	6.9	2.0	-	9.2	-	0.002	0.18	0.01	0.35	0
	781013	4.36	88	7.9	1.9	-	8.5	6.9	-	0.36	0.02	0.39	0
	790515	4.27	76	7.5	2.0	-	8.5	-	0.014	0.47	0.29	0.71	0
L 5	771012	4.06	43	10.6	2.5	1.4	16.0	-	-	0.8	0.04	0.04	0
	780428	4.31	18	8.4	2.9	-	14.4	5.3	0.020	0.64	<0.03	0.05	0
	780821	4.60	28	10.8	6.0	-	19.2	-	0.016	0.62	0.03	0.07	0
	781013	4.55	22	7.3	2.0	-	13.3	7.6	+	1.1	0.07	0.11	0
	790515	4.15	17	10.0	2.5	-	17.1	-	0.006	0.99	0.029	0.28	0

[1] No explanation for '+' given in original table.

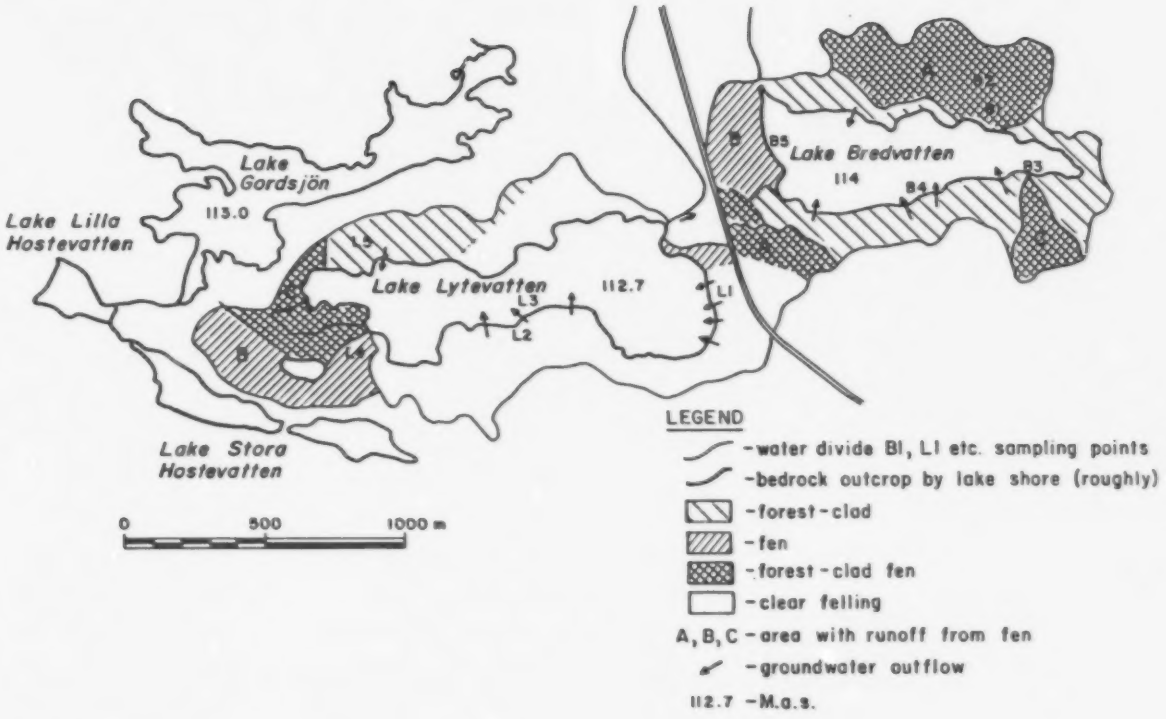

Figure 31. Location of sampling points, Bredvatten, Sweden. Source: Hultberg and Johansson (1981)

Further downstream in the valley, low pH and high metal content was found in two main areas both with shallow aquifers. Inflow from a farmed area (not lime treated) had pH 3.6-4.6 and an aluminum content of 7.6-1.6 mg/L, and groundwater from an older marsh had a pH value of 3.6-5.4 and an aluminum content <1.6-0.2 mg/L.

Even in areas of igneous bedrock, larger streams are essentially not affected by acid precipitation because of a two-step neutralization process (Johnson 1979). The first step of this process consists of neutralization of acid rain in the upper soil by dissolution of pre-existing aluminum hydroxide compounds and by leaching of bases from biological matter so that rain has already been neutralized to a great extent before it reaches the stream. This neutralization is accompanied by high leaching losses of aluminum to the stream (Cronan and Schofield 1979; Johnson 1979). As the water moves downstream, the second step occurs. This step consists of chemical weathering reactions with loss of aluminum and gain of strong bases and silica by the water.

Temporal data are, of course, of special interest but seem to be scarce. Troedsson (1955, cited by Nilsson and Bergkvist 1983) reported pH values and Al concentrations in groundwater from a number of Swedish forest localities, although none of them was characterized by the very thin soils found in the Gordsja catchment. pH values were mostly above 6.0 and the Al concentrations were accordingly very low. Some samples had pH <6.0 and Al concentrations in the order of 10 x 20 moles L^{-1}, but such results were invariably connected with high amounts of dissolved organic matter.

It does not seem unreasonable to claim that the observed high concentrations of mainly inorganic Al forms in soil solution and shallow groundwater constitute a fairly new phenomenon. Atmospheric deposition of acid compounds is likely to be one important reason for the observed phenomenon (Nilsson and Bergkvist 1983).

2.5.2 Other Metals

A study of well water quality in the Adirondack Mountains of New State by Fuchs and Olsen (1979, cited by Sibul and Vallery 1982) revealed excess concentrations of some trace metals in drinking water. The source of these metals was related to leaching from natural bedrock and overburden formations, and to leaching from metal piping in household water distribution systems. Copper and lead levels were found to be notably high in some domestic water supplies with low pH and alkalinity values. Aluminum levels were found to be high in some spring-derived water samples, indicating a natural source of aluminum.

In Sweden, the sudden appearance of metals (Al, Mn, Fe, and to some extent Zn, Cu, Cr, and Cd) in the water of Stenunge Stream and metal precipitates in sediments has severely affected sea trout reproduction along 72 km of the stream (Hultberg and Johansson 1978). Downstream on Stenunge Stream, inflow of groundwater with a higher pH (>6.0) from deeper aquifers has continuously increased the pH of the stream water and caused precipitation of the metals.

pH versus metal contents of all analysed groundwater samples from different aquifers and sampling depths in the Stenunge basin are summarized in Figures 32 and 40 (Section 2.9.2). The graphs show that while pH decreases to approximately 5, other elements increase exponentially with further reduction of the pH. The theoretical calculations of aluminum dissolution from soil with decreasing pH (Eriksson 1979, cited by Hultberg and Wenblad 1980) agree with this data.

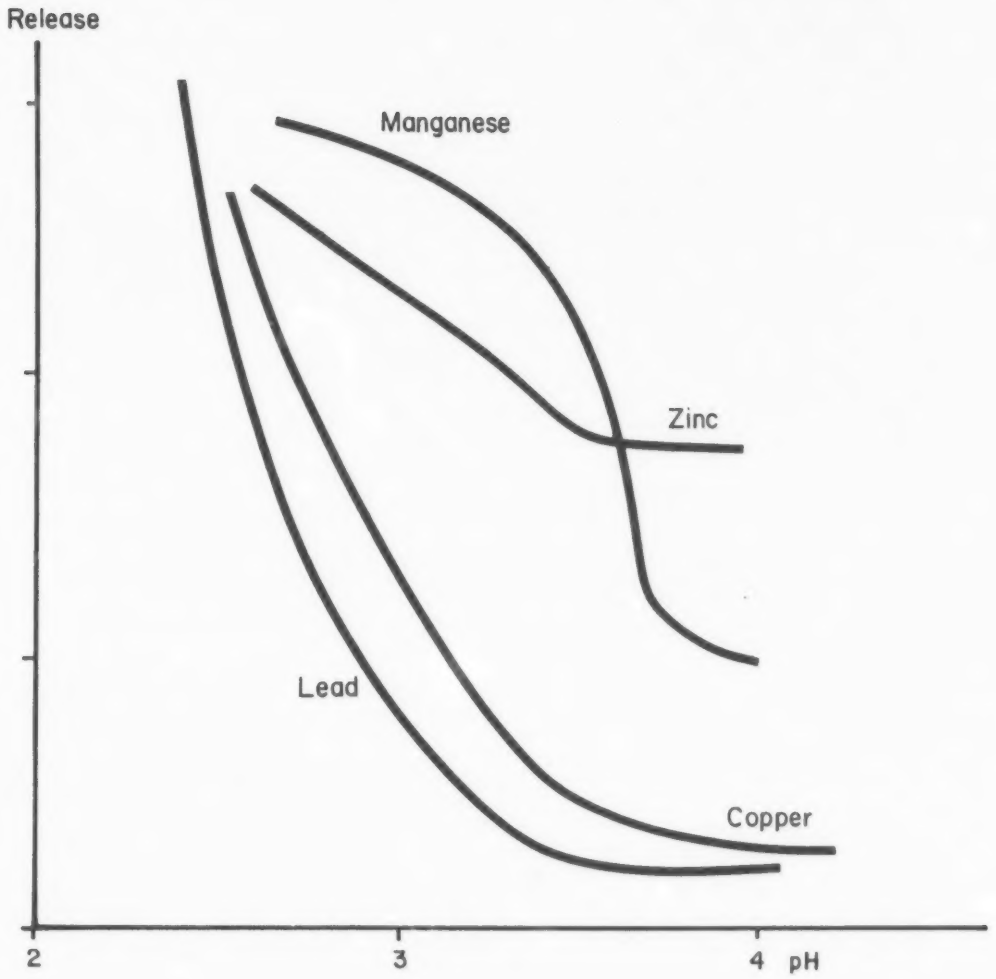

Figure 32. Release of zinc, manganese, copper, and lead from enrichment layer at various pH levels. Source: SNV (1981), in Swedish Ministry of Agriculture (1982)

In Delaware, Sparks and Curtis (1983) examined the acid rain and the kinetics of elemental release in three soil types. All three soils contained low clay and organic matter contents which would indicate rather low buffering capacities. The report indicated that the action of acidic deposition on soil is very rapid and that the release of metals is almost instantaneous. Equilibrium release of elements was realized for all elements. The study by Sparks and Curtis suggested that the impact of acidic deposition on groundwater may be episodic in nature with major impacts occurring during the spring thaw period or during intense rainfall events.

These results appear to be in agreement with Wiklander (1980), who concluded that the rate of leaching of NO_3^-, SO_4^{2-}, and heavy metals into the groundwater may be increased by acid precipitation.

In Alberta, Campbell et al. (1984) found that no significant mobilization of metals had occurred from a till material that had been exposed to very low pH (1-3) for a period of 10-15 years. However, elsewhere in Alberta, Campbell (unpublished data) has noted elevated arsenic levels in groundwater with pH values in the 6.5-8.0 range. Based on these observations it is suggested that pH may not be as reliable an indicator of the mobility of metals as has been previously accepted.

Experiments on lake sediments from Sagamore Lake and Woods Lake show that in the range of pH 1 to 3 considerable lead is released (Figure 33). However, these release curves are similar in form to immobilization (adsorption) curves noted by other workers (Fuerstanan et al. 1970; Brown 1979), but the desorption edge is approximately 2 to 3 pH units lower than predicted by current models or systems with one adsorbing component. However, these results are consistent with the work of Lagerwerff et al. (1976) who, in a series of extraction experiments using Baltimore sewage sludge containing 531 mg Pb g^{-1} sediment, released only 0.02% (0.1 µg Pb g^{-1}) at pH 5.2 and 0.11% (.51 µg Pb g^{-1}) at pH 3.8. Unfortunately, this latter pH was the lowest chosen.

These results, together with data presented in this paper, suggest that lead release from the sediment into groundwater or overlying surface water occurs at a pH lower than was previously anticipated. The pH values of Sagamore and Woods Lake sediment (pH 6.0-6.5 and pH 5.6-6.0, respectively) are too high for release into the pore water, while the pH of the lake is currently above that which would result in measureable release of lead from the sediment into the overlying water.

It should be noted that no lead minerals were observed in either watershed. It is therefore concluded that the source of the lead is atmospheric.

The rates of metal accumulation in the Woods and Sagamore Lakes sediments have been estimated to typically be 100 to 600, 50 to 300, 10 to 60, and 5 to 30 mg m^{-2} y^{-1} for Ni, Cu, Zn, and Pb, respectively. The enrichment factors for metals in surficial sediments typically are 12 to 115 for Ni, 10 to 77 for Cu, 2 to 10 for Pb, and 2 to 8 for Zn. These enrichment factors and deposition rates for Ni and Cu are among the highest recorded anywhere in the world. Some of the lakes with pH values of 4.5 or less show an enrichment or accumulation of pollutant metals in their surface sediments, indicating that pollutant metals previously stored in the sediments have since been leached away. This documentation that the contaminated sediments can release substantial quantities of toxic metals to the overlying water must have interesting ramifications with regard to the limnological impacts of acid rain. Similarly, groundwater mobilized metals which

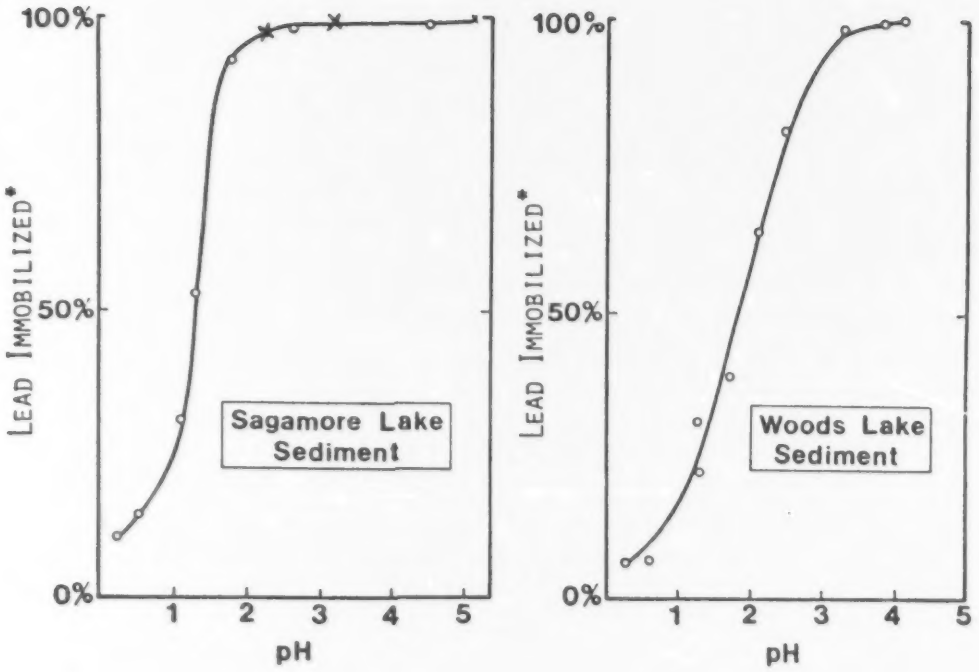

Figure 33. Release of lead from the sediment of Sagamore and Woods Lakes. Small circles represent HNO_3 used in experiment. Small "x" represents H_2SO_4. Source: Davis (1983)

are temporarily adsorped in the subsurface could be mobilized by pulses of highly acidic recharge or at the eventual exhaustion of the basin acid neutralization capacity.

Gatz et al. (1984) studied the solubility of metals in both dry and wet atmospheric deposition. They contended that the solubility of metals is a function not only of pH, but also of the influence of organic materials, clay minerals, metals hydroxides, and divalent ions.

Metal solubility decreased with increasing concentrations of both TIM (an index of the clay minerals) and insoluble Fe. Zn and Cd were the most soluble, followed by Cu and Pb in both sets of observations. The observed order agrees with similar observations of metal ion affinities for montmorillonite, kaolinite, and illite as reported by Farrah and Pickering (1977). The overall order of mobility and bio-availability of the same metals in street dust and roadside soils analysed by Harrison et al. (1981) was somewhat different: Cd>Pb = Zn>Ca. Metal solubility in precipitation is similar to that of other natural waters; that is, solubility decreases as pH and the concentrations of total mass and insoluble Fe increase.

2.6 ROLE OF GROUNDWATER HYDROLOGY IN THE ACIDIFICATION PROCESS

Early assessments of groundwater acidification noted the relationship between permeability, well depth, and pH (Hultberg and Johansson 1981; Sibul and Vallery 1982; and Soveri 1982). Henriksen and Kirkhusmo (1982) observed that, in Norway, acidification was taking place in the upper part of the groundwater zone. Skartvelt and Gjessing (1979), in their examination of surface water chemistry in Norway, concluded that certain carbonic changes in surface water chemistry are probably linked to changes in the contact of water with soils and residence time in various geological zones within the catchment.

The NHP Working Group for Groundwater Networks concluded that the pH of groundwater depends on:

1. the amount and pH of precipitation;
2. the weathering of the bedrock and the minerals of the unconsolidated deposits;
3. the physical properties of the bedrock and the unconsolidated deposits;
4. the residence time of the water in the bedrock and or unconsolidated deposits; and,
5. the ratios of alkaline and acidic minerals in the bedrock and unconsolidated deposits.

Even Rosenqvist (1978), who disputes the causes of acidification, concluded that the nature of the geological material and the time of contact are regarded as decisive factors for the chemical reactions which take place in a catchment area.

Recent studies (ILWAS) of groundwater chemistry in two mineralogically similar basins (Tetra Tech Inc. 1984) in the Adirondacks of New York State have concluded that the routing of water through different flow paths within a watershed is a major determinant of a lake's alkalinity and its vulnerability to acidification by atmospheric deposition. The results of this study, which is to date the most detailed examination of the processes controlling acidification of the environment, show that the influence

of hydrology on the sensitivity of a particular ecological setting to acidic deposition has been underestimated. The ILWAS results seem to be supported from a hydrologic standpoint by the results of Fritz et al. (1976) which showed that in three small watersheds, groundwater runoff constituted 32% to 42% of peak basin discharge. Eilers et al. (1983), following an assessment of 257 lakes in Wisconsin, concluded that hydrologic factors were most important in differentiating the low alkalinity and high alkalinity lakes.

In Canada, Bottomley et al. (1984), in an examination of watersheds on the Precambrian Shield of Ontario, also concluded that storm runoff in the study basins consists of 40% to 90% groundwater, depending on rainfall amount and intensity, antecedent soil moisture conditions, and water table depth.

Jackson and Patterson (1982) described a two-step neutralization process of acid precipitation recharging the groundwater system. The process is intimately tied to position along the flow path and, hence, a detailed understanding of the groundwater regime is necessary to the development of this model.

The importance of groundwater velocity flow path in the assessment of impact by acidic deposition on lakes has been recognized by the European researchers (Johansson and Hultberg 1977, cited by Hultberg and Johansson 1981; Rosenqvist 1978; Hultberg and Johansson 1981; and Nilsson and Bergkvist 1983).

Jackson and Patterson (1982) showed that the groundwater chemistry in an artificially acidified fluvial sand aquifer near Chalk River, Ontario is largely a function of flow path and residence time. A two-step neutralization process was recognized, similar to that described by Johnson (1982) in which the first step is the dissolution of soil zone alumina and the second is the alteration of silical minerals. Bottomley et al. (1984) concluded after studying Turkey Lake and Harp Lake watersheds in central Ontario that groundwater discharge to streams in the Harp Lake watershed has a major ameliorating influence on the acid input to Harp Lake. It was further concluded that should the neutralizing capacity of the surficial deposits become exhausted, the groundwater will become acidified as has been observed in Norway (Henricksen and Kirkhusmo 1982). If this occurs, the groundwater component of storm runoff will cease to have an ameliorating influence on acid precipitation, and surface water acidification will worsen. The capacity of lake sediments to neutralize surface water has been discussed by Oliver and Kelso (1983), and others.

Hongve (1977) and other Canadian researchers (Eilers et al. 1983) have concluded that the one important factor that susceptible lakes have in common across regions is a minimal groundwater input. Thus, the challenge of accurately assessing lake susceptibility, in part, will be to quantify lake/groundwater interactions.

Investigations using artificial acid treated irrigation water over a two year period at a lake site in north central Florida (Volk and Byers 1983) suggested a relatively high and rapid loss of nutrients from the soil surface to the water table 4 m below, under acidic irrigation conditions. Most of the applied water, regardless of the amount, was lost from the soil site to the water table after 48 hours. Lateral movement in the groundwater to the lake was likewise very fast due to the high hydraulic conductivity of the soil. There was essentially little non-vertical flow to the water table and horizontal movement towards the lake was rapid. The effect of the acid treatments from a very large rain event could be observed in the groundwater near the lake within 24 hours.

The Laurel Hill study (Sharpe et al. 1984) showed a clear inverse relationship between stream alkalinity and discharge, and between stream pH and discharge can be seen in all four streams studied (Figures 34 and 35). At the onset of snowmelt, the pH dropped sharply in Wild Cat, McGinnis, and Linn runs as soon as stream discharge began to increase. This initial input of H^+ has been explained in previous investigations (Johansson and Henricksen 1978; Siep 1980) which have shown that when impure snow and ice melt slowly, most of the impurities are found in the first fractions of the meltwater.

The hydrogeology of the Laurel Hill basins, especially the burial depth, dip, and strike of the Loyalhanna Limestone Formation, exert a major control on the natural baseflow chemistry and the buffering capacity of the streams (Chen et al. 1983). The resistant Pocono Sandstone underlies much of the study area and a highly permeable rocky soil overlies the bedrock. Infiltration rates are high and a large percentage of the snowmelt reaches the channel by way of shallow groundwater flowing at the soil/bedrock interface rather than by subsurface flow in soil. The large, shallow groundwater storage capacity in Cord Machine Run Basin was not satisfied until around February 18, 1981, at which time a runoff increase began to shown in the stream as well as an increase in acidity to the same levels as the Linn and McGinnis runs (Figure 35).

The ILWAS project has undertaken the most detailed examination of acidic deposition as it relates to groundwater chemistry. The study clearly demonstrated that the acid-base status is determined by the interaction of many factors (e.g., soil, hydrology, vegetation, geology, climatic, atmospheric) and that the relevant role of any one factor can be highly variable geographically (even within a region as small as that defined by the ILWAS site) and temporally. However, hydrologic and chemical analyses lead to the general conclusion that the relative routing of water through a watershed is a major determinant of lake water alkalinity and vulnerability to acidification by atmospheric deposition. A lake may be located in a watershed underlain with readily weatherable alkaline rock (e.g., limestone), but if the water flowing into the lake is isolated from the rock by impermeable soils, then the rock cannot supply alkalinity to the lake. The difference in acid status between Woods and Panther Lakes and the snowmelt acid pulse can both be explained by flowpath analysis. Panther Lake was more alkaline than Woods because water flowing through the deep soils made a greater relative contribution to its inflow (Figure 36). Cation exchange and mineral weathering, the major sources of base cations and, hence, alkalinity in the ILWAS watersheds were in the deeper inorganic soil. For the ILWAS study sites, the relative contribution of the deep soil flow path is directly correlated to soil depth (Figure 36).

The chemical characteristics of the soil solutions in a given horizon in Woods Lake are virtually indistinguishable from those in the same horizon in Panther Lake. The differences in lake acidity between these two systems cannot be explained on the basis of contrasts in the solution characteristics of any given layer.

The differences in acidification of Woods and Panther Lakes have been directly linked to differences between the surficial geology of the watersheds (April and Newton 1984). Although the surficial deposits occupying both basins are mineralogically and texturally similar, they differ significantly in thickness and permeability. Consequently, the flow paths along which precipitation moves enroute to the lake and the amount of acid neutralization that occurs, are markedly different in each watershed.

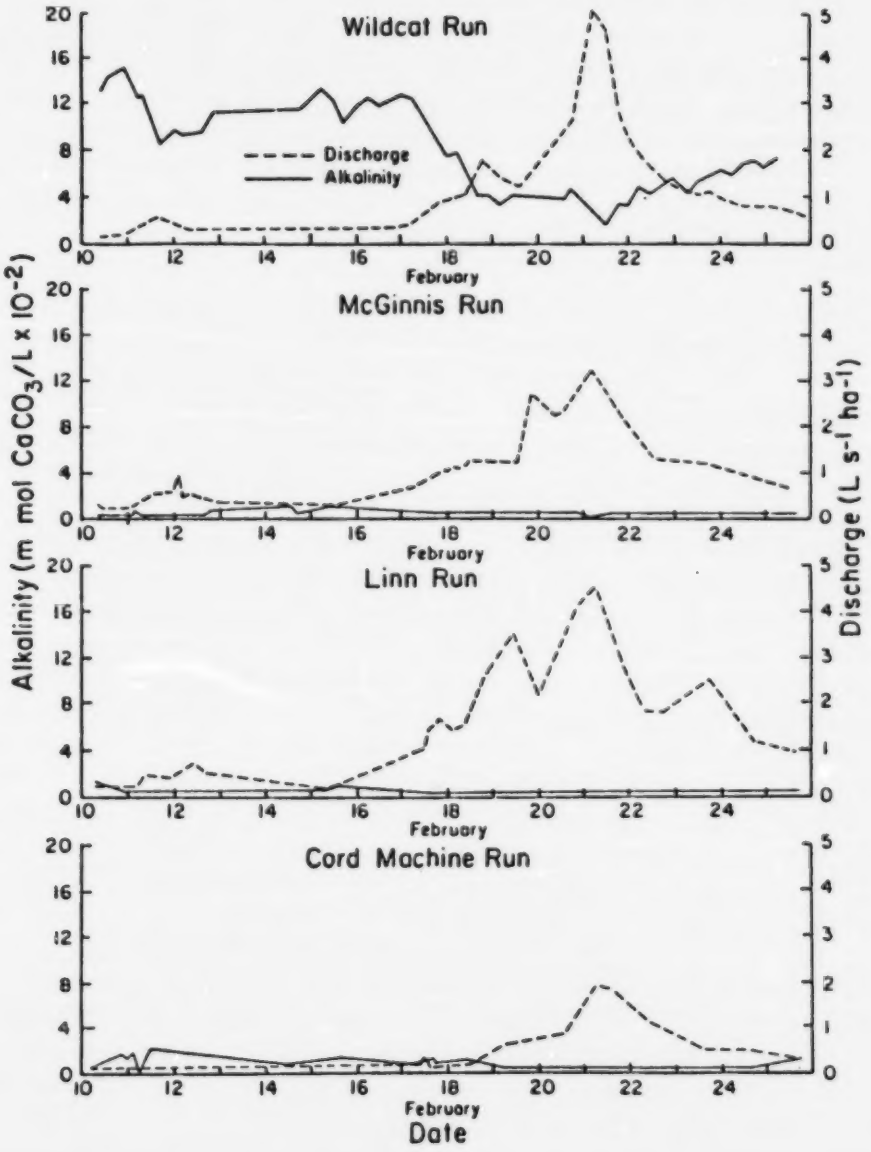

Figure 34. Comparison of stream alkalinity and discharge on four Laurel Hill basins during a major season runoff event, 1981. Source: Sharpe et al. (1984)

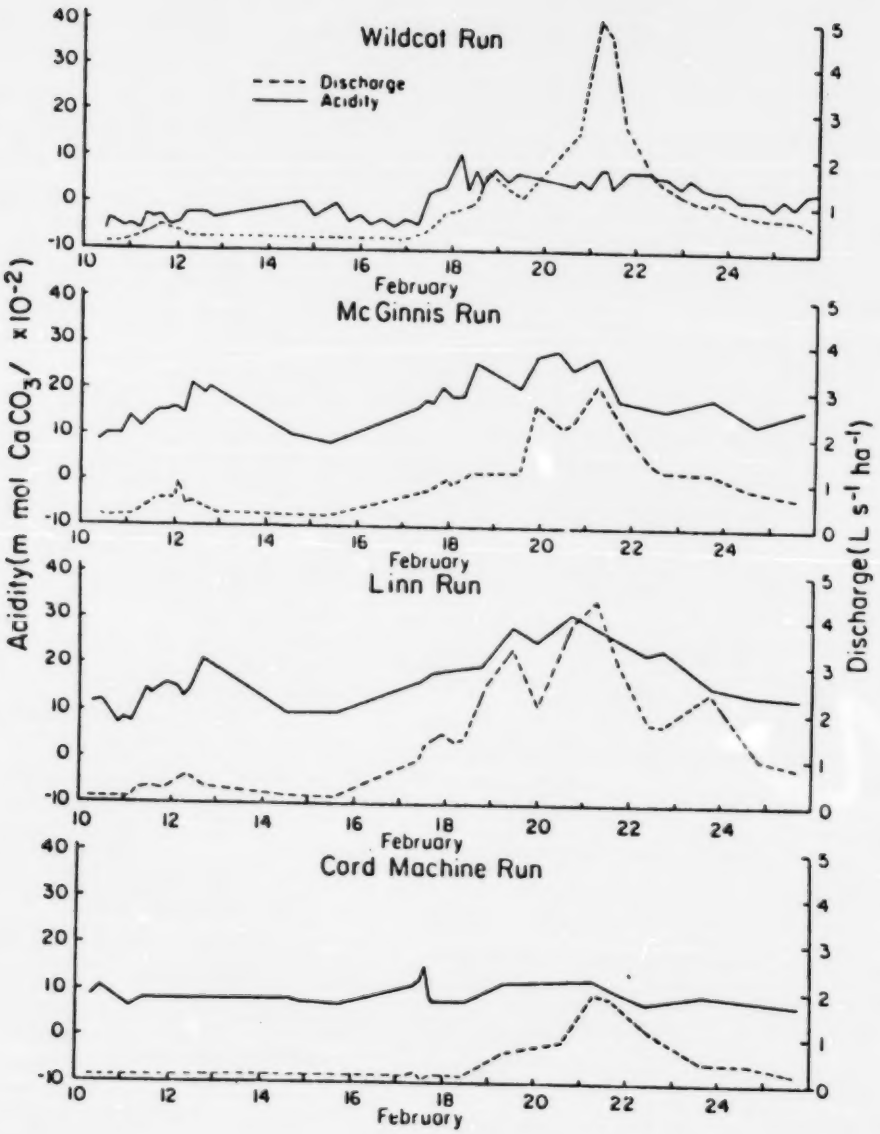

Figure 35. Comparison of stream acidity and discharge on four Laurel Hill basins during a major dormant season runoff event, 1981. Source: Sharpe et al. (1984)

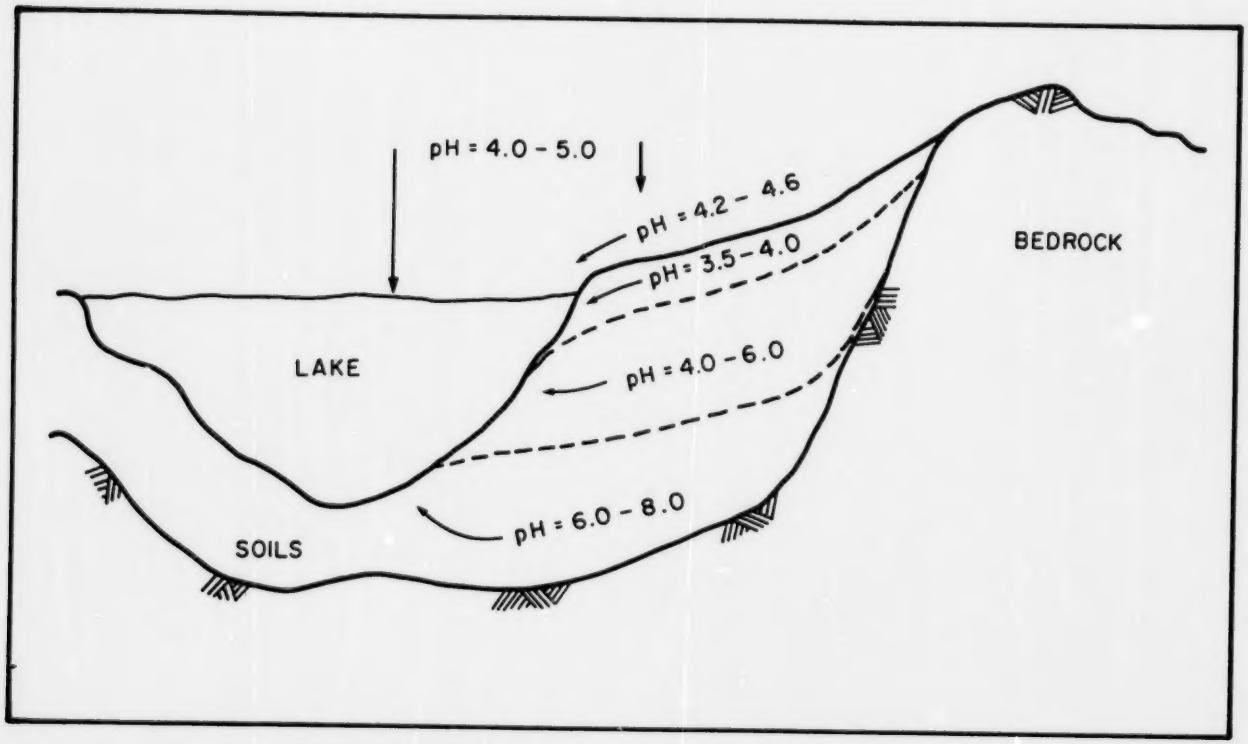

Figure 36. Importance of groundwater flow regime in determining lakewater pH. Source: Chen et al. (1983)

The longer residence time of water in the groundwater system of Panther Lake allows the rate-limited neutralization reactions such as primary mineral weathering to proceed further towards completion. Sufficient acid neutralization take place to keep the water of Panther Lake near a pH of 7 for most of the year. Only during the annual spring melt, when a large portion of water enters the lake through overland flow and shallow interflow, does the pH of Panther Lake surface water drop to approximately 5.

The application of sulphuric acid on soil has been related to an increase in infiltration rates and, thus, may result in increased recharge to the groundwater portion of the hydrologic regime. In one greenhouse experiment carried out on a soil from California (Overstreet et al. 1951), the effects of three rates of sulphuric acid and 5.6 t/ha of gypsum on percolation rates were compared. The results are shown in Tables 7 and 8. All rates of applied sulphuric acid increased the percolation rate of water. In this experiment, the acid was added to the soil and the leaching water subsequently applied. Under field conditions, the application of sulphuric acid to soil resulted in improved crop yields. The improvement in yield has been attributed to improved soil structure and increased water penetration. Similar results were observed in studies conducted in Arizona, California, and Texas (Robinson et al. 1968; Miyamoto and Stoehlein 1975; and Yahia et al. 1975).

The implication of these findings is that the chemical interaction between acidic deposition and the soil may significantly increase the rates of groundwater recharge and thus alter the hydrologic balance. While the possibility of widespread impacts seems remote, the possibility of local impacts is a possibility and should not be discounted.

It has been widely accepted that vegetation cover has a pronounced influence on basin hydrology. Changes in vegetative cover in a basin may result in changes in runoff and infiltration characteristics. These altered basin characteristics may be reflected in changes in physical and chemical characteristics of both surface water and groundwater as well as in the basin hydrograph. Ward (1967) cited an example in the Vyrnwy catchment in Wales (Figure 37). In the non-forested area the hydrograph rises markedly during rainfall and falls rapidly when the rain ceases; in the forested area, the peak rates of discharge are much lower and the falling limbs of the hydrograph have a much more gentle shape suggesting ponding of surface water and its later slow release.

Certainly if the "dieback" of vegetation observed in Europe and eastern North America were to occur on a regional scale in Alberta, there would undoubtedly be major disruption of basin characteristics.

2.7 SENSITIVITY ANALYSIS

Since the time the phenomena of acidic deposition was recognized, attempts have been made to predict the impact of such deposition on the terrestrial environment. Most of the early work focussed on the acidification aspects and therefore much emphasis was placed on pH measurements and the capacity of a soil or bedrock material to neutralize acid. Soil scientists tend to consider the water table to be a "sink" for soil leachate rather than a component in the hydrologic cycle.

Early investigators considered bedrock geology to be a reasonable indicator of the long-term susceptibility of an area to acidification by precipitation. Using bedrock

Table 7. Rate of water percolation through buckets of soil taken from the reclamation plots near Kerman, CA. Experiment carried out in greenhouse at Berkeley.

Treatment	Period of Leaching	Volume of Percolate (Average)	Percolation Rate at End of Leaching Period
Untreated	5 Weeks	20.1 Litres	0.17 Litres/day
0.80 Tonnes H_2SO_4/ha	5 Weeks	24.4 Litres	0.24 Litres/day
1.59 Tonnes H_2SO_4/ha	5 Weeks	27.3 Litres	0.47 Litres/day
3.18 Tonnes H_2SO_4/ha	5 Weeks	31.0 Litres	0.57 Litres/day
5.62 Tonnes Gypsum/ha	3 Weeks	19.0 Litres	0.17 Litres/day

Source: Stromberg and Tisdale (1979)

Table 8. Effect of water-applied sulphuric acid on steady-state infiltration rates.

Water Source	Well Water	Salt River	Well Water	Rio Grande
Locations	Yuma	Phoenix	Safford	El Paso
Water class*	C4-S3	C3-S2	C2-S2	C3-S1
TDS, mS/cm	3.9	1.3	0.7	1.2
SAR	8.4	6.3	7.2	3.8
Bicarbonate, ppm	300	165	170	200
Acid rate, ppm	230	110	100	150
pH before treatment	8.0	8.2	8.6	8.2
pH after treatment	7.9	7.9	7.8	8.0
		Infiltration Rate (cm/day)		
Sonoita sandy loam				
No acid	50	33	27	51
Acid	57	49	45	53
Anthony sandy loam				
No acid	35	24	18	36
Acid	40	34	30	37
Cave loam				
No acid	22	18	17	24
Acid	25	20	19	24
Grabe clay loam				
No acid	8.9	5.9	2.9	7.8
Acid	10	6.8	5.4	8.0

* Water class - see USDA Handbook 60 (Richards 1954) Source: Stromberg and Tisdale (1979)

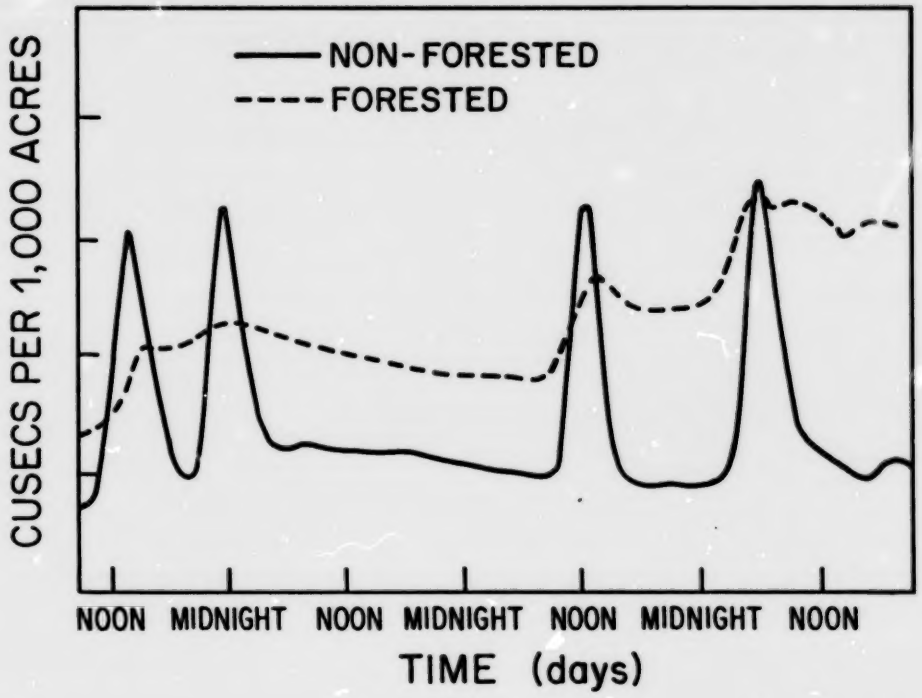

Figure 37. Stream hydrographs for two areas of the Vyrnwy catchment in Wales. Source: Ward (1967)

geology as an indicator, Galloway and Cowling (1978) mapped those areas of North America that have a potential for being sensitive to acidic precipitation. The shaded areas in Figure 38 indicate bedrock composed of igneous or metamorphic rock, whereas unshaded areas are calcareous or sedimentary rock. Igneous or metamorphic bedrock weathers slowly; therefore, lakes in these areas would be assumed to have low alkalinity and low buffering capacity.

Glass et al. (1982) classified rock formations by their ability to neutralize acid. Table 9 lists the four major types of rock formations. Alkalinity levels of less than 200 meq/L have been associated with Type I and Type II rock formations. It was recognized by Glass et al. (1982) that attempts to classify regions by sensitivity to acidic precipitation must take into account the potential buffering capacity of rock mixtures and the types of surficial materials overlying formations, as the soils do not necessarily have the same composition as the bedrock below. The soil's cation exchange capacity and the ability to retain sulphates are good indicators of an area's sensitivity to acidic precipitation. The cation exchange capacity and the corresponding level of soil sensitivity are listed in Table 10.

The task of generating a sensitivity map of northern Alberta and northern Saskatchewan has been undertaken by the Saskatchewan Research Council. The bedrock in the study area has been divided into four sensitivity (buffering) capacity classes following a similar classification undertaken in eastern Canada (Shilts 1980, cited by Saskatchewan Research Council 1981) (Table 11). In assessing the sensitivity of soils, it was concluded that the level of a soil's sensitivity reflects the integrated result of several factors, of which buffering capacity and pH are the most significant. In this study, cation exchange capacity (CEC) is used to estimate the buffering capacity in mineral soils:

1. Most sensitive soils
   - Low Buffering Capacity: CEC $\leq$6 meq/100 g soil
2. Soils of intermediate sensitivity
   - Medium Buffering Capacity: CEC = 6 to 15 meq/100 g soil
3. Least sensitive soils
   - High Buffering Capacity: CEC $\geq$15 meq/100 g soil

This basic system was subsequently expanded to include seventeen sub-categories. A review of the maps generated using this methodology shows that the bedrock materials of Silurian age or younger are considered to have low to low-intermediate sensitivity. Cambrian bedrock and some unconsolidated quarternary deposits are considered to be of intermediate to high sensitivity.

On the other hand, soil materials in northeastern Alberta range from most sensitive to least sensitive. Most soils, however, are classified as having high to intermediate sensitivity. The results of the soil sensitivity assessment are similar to the results of Shilts (1980) in eastern Canada. Due to the difference in the area of exposed Precambrian rock in Alberta compared to Quebec, there is a significant difference in bedrock sensitivity.

Figure 38. Regions in North America which may be sensitive to acid precipitation, using bedrock geology as an indicator. Source: Galloway and Cowling (1978)

Table 9. Classification of rock formations according to their ability to neutralize acid.

	Class	Alkalinity (meq/L)
1.	Acidified	0
2.	Extreme Sensitivity	0-39
3.	Moderate Sensitivity	40-199
4.	Low Sensitivity	200-499
5.	Not Sensitive	≥500

Type I Low or no buffering capacity, overlying waters, very sensitive to acidification (granite/syenite, granitic gneisses, quartz sandstones, or equivalents)

Type II Medium-to-low buffering capacity, acidification restricted to first and second order streams and small lakes (sandstones, shales, conglomerates, high grade metamorphic to intermediate volcanic rock, intermediate igneous rocks, calc-silicate gneisses).

Type III High to medium buffering capacity, no acidification except in cases of overland runoff in areas of frozen ground (slightly calcareous, low grade intermediate to mafic volcanic, ultramafic, glassy volcanic rocks)

Type IV "Infinite" buffering capacity, no acid precipitation effect of any kind (highly fossiliferous sediments or metamorphic equivalents, limestones, dolostones)

Table 10. Soil sensitivity to acid precipitation.

Sensitivity	Cation Exchange Capacity (CEC) meq/100 g soil	Other Relevant Conditions
Nonsensitive	Any value	Free carbonate present or subject to frequent flooding
	> 15.4	None
Slightly Sensitive	6.2 ≤CEC ≤15.4	Free carbonates absent; not subject to frequent flooding
Sensitive	<6.2	Free carbonates absent; not subject to frequent flooding.

Source: Glass et al. (1982)

Table 11. Sensitivity of bedrock material.

Type A	HIGH SENSITIVITY (LOW BUFFERING CAPACITY)
	Precambrian sedimentary cover - Athabasca Sandstone Formation, quartzitic sandstone to conglomerate with minor silt and clay interbeds.
	Quarternary deposits - extremely sandy deposits, discontinuous cover of variable thickness.
Type B	INTERMEDIATE-HIGH SENSITIVITY (INTERMEDIATE-LOW BUFFERING CAPACITY)
	Precambrian basement complex - Plutonic rocks mainly granite, granodiorite, and quartz monzonites with various amounts of metasediments, metavolcanics, and some mafic and ultramafic rocks.
	Quarternary deposits - very sandy deposits with silt and clay in southeast part, very discontinuous cover of variable thickness.
Type C	INTERMEDIATE-LOW SENSITIVITY (INTERMEDIATE-HIGH BUFFERING CAPACITY)
	Cretaceous - shales, sandstone, interbedded or interspersed with other calcareous, noncalcareous, and carbonaceous sedimentary rocks.
	Quarternary deposits - clay and carbonate rich deposits, thick, nearly continuous cover.
Type D	LOW SENSITIVITY (HIGH BUFFERING CAPACITY)
	Silurian and Devonian - limestone and dolomites.
	Quarternary deposits - clay and carbonate rich deposits, thick, continuous cover.

Source: Shilts (1980), in Saskatchewan Research Council (1981)

A weakness in attempts to determine sensitivity to date is that the procedures tend to look at the geological medium in isolation. That is, little consideration is given to the role of groundwater movement in the assessment of sensitivity. For example, it is intuitively recognized that the penetration of acid precipitation in a groundwater discharge area will be very much less than the penetration of acidic deposition in a recharge area. As well, products of leaching may move rapidly into the groundwater regime and become a problem, not at the point of application of acid, but at the point of ground discharge. Indeed, many of the present groundwater problems on the prairies are related to salt build up in areas of groundwater discharge.

Another primary weakness in the sensitivity studies undertaken is that they only consider acidification as reflected by pH. No consideration is given to the capacity of a particular geological setting to generate leachates that result from the acid neutralization process or the impact these leachates may have on the chemical quality of groundwater in a particular area. While several authors in their discussion of sensitivity have alluded to the impact on groundwater chemistry of cross-formational flow, this discussion is generally in the context of discussing the buffering capacity of thin, calcareous drift overlying Precambrian Shield type deposits.

2.8 MODELLING

Understanding the interaction of groundwater and surface water is a key factor in understanding and assessing the impact of acid precipitation on aquatic resources. Numerous papers published recently have discussed the impacts of acidic deposition on aquatic and terrestrial ecosystems. However, few papers have addressed the interaction of groundwater and surface water and no paper has discussed a rigid physically-based model of the complete continuum from land surface through the soil zone, unsaturated zone, and groundwater zone, to a surface water body.

Modelling has been demonstrated to be an effective tool in dealing with complex geological and groundwater problems. Historically, three types of models have been utilized: physical, analytical, and numerical. The physical model is intuitively obvious and will not be dealt with in detail. The analytical and numerical models are more powerful tools in dealing with complex problems. This is not to underemphasize the importance of the physical model, as numerical models can seldom be used effectively without having first established a physical model or framework. Although mathematically exact, analytical models can be applied only to simple one-dimensional or greatly simplified two-dimensional problems because of the rigid boundary conditions and simplifying assumptions. Nevertheless, they have proven useful in evaluating many field problems. In comparison, numerical models have proven more useful.

A number of numerical models have been developed that simulate the impact of acidic deposition on groundwater. The most complex model assembled to date is the ILWAS model. This a deterministic model developed to calculate surface and groundwater chemical characteristics given watershed and time-varying inputs such as precipitation quantity and quality, and ambient air quality. The essence of the model is to route water from one compartment to another and to calculate the concentrations of dissolved chemical constituents by simulating the biogeochemical reactions taking place in each compartment. The ILWAS model has been developed so that one can perform the hydrologic

simulation alone, or hydrologic and chemical processes can be simulated simultaneously and monitored at any convenient point of the system (Figure 39).

A less complex model (Booty and Kramer 1984) includes a hydrologic and geochemical component, but does not include a biological or microbiological fraction. This model has been successful in predicting long-term fluctuations in pH.

Christophersen et al. (1982) have developed a relatively simple model based on hydrologic and geochemical components. The hydrologic sub-model is a two-reservoir model worked out by Lundquist (1976,1977). The upper reservoir supplies quick flow and can be thought of as water mainly in contact with or having its last contact with the upper soil horizon. The lower reservoir provides the baseflow. Although the chemical processes incorporated in the geochemical sub-model include cation exchange, weathering, dissolution/precipitation of gibbsite, sulphate adsorption/desorption, and sulphate mineralization, the model is designed to simulate stream water chemistry. A weakness in the model is its inability to represent complex geological settings. Although the roles of K, NH_4, NO_3, and HCO_3 are ignored, the major ions H, Ca, Mg, Al, and SO_4 are considered. Based on a cursory overview of available models it is suggested that the geochemical models most likely to be of use to the ADRP are PHREEQE, GEOCHEM, GEOCHEM II, and ILWAS.

2.9 HUMAN IMPACT

Evidence presented to date indicates that there are identifiable issues regarding the potential human effects of acidification of groundwater.

The two major areas of concern are: (1) the leaching of toxic chemicals from watersheds and from water storage and distribution systems, leading to the contamination of drinking water supplies; and (2) the contamination of edible fish by toxic chemicals, principally mercury.

The source of concern is the fact that solubility of many metals such as lead, copper, cadmium, and aluminum increases sharply with decreased pH. Acidic groundwater can thus leach metals from the soil, from lake sediments, from metal pipes used in water systems, and from soldering materials used to join pipes. It can also free calcium ions and asbestos fibers from cement. The attack of water pipes by acidic groundwater is at present the corrosion problem that is most evident in this context. In recent studies conducted in Sweden, of 1190 shallow wells investigated in six provinces, 31%-76% showed pH values <6. The technical and economic aspects of corrosive water are obvious.

The New York State Department of Health has also linked acid rain to outbreaks of gastroenteritis in the Adirondack Mountains. They traced the disease to acid resistant strains of bacteria found in wells fed by acid groundwater.

Aspects of these various potential impacts on humans are discussed in more detail below.

2.9.1 Mercury

The most thoroughly studied metal in the environment is probably mercury, which has been shown to accumulate in fish. There is evidence to suggest that fish populations in poorly buffered waters with subnormal pH have elevated levels of mercury in their tissues. Although acid rain is not the sole cause of the environmental problems related

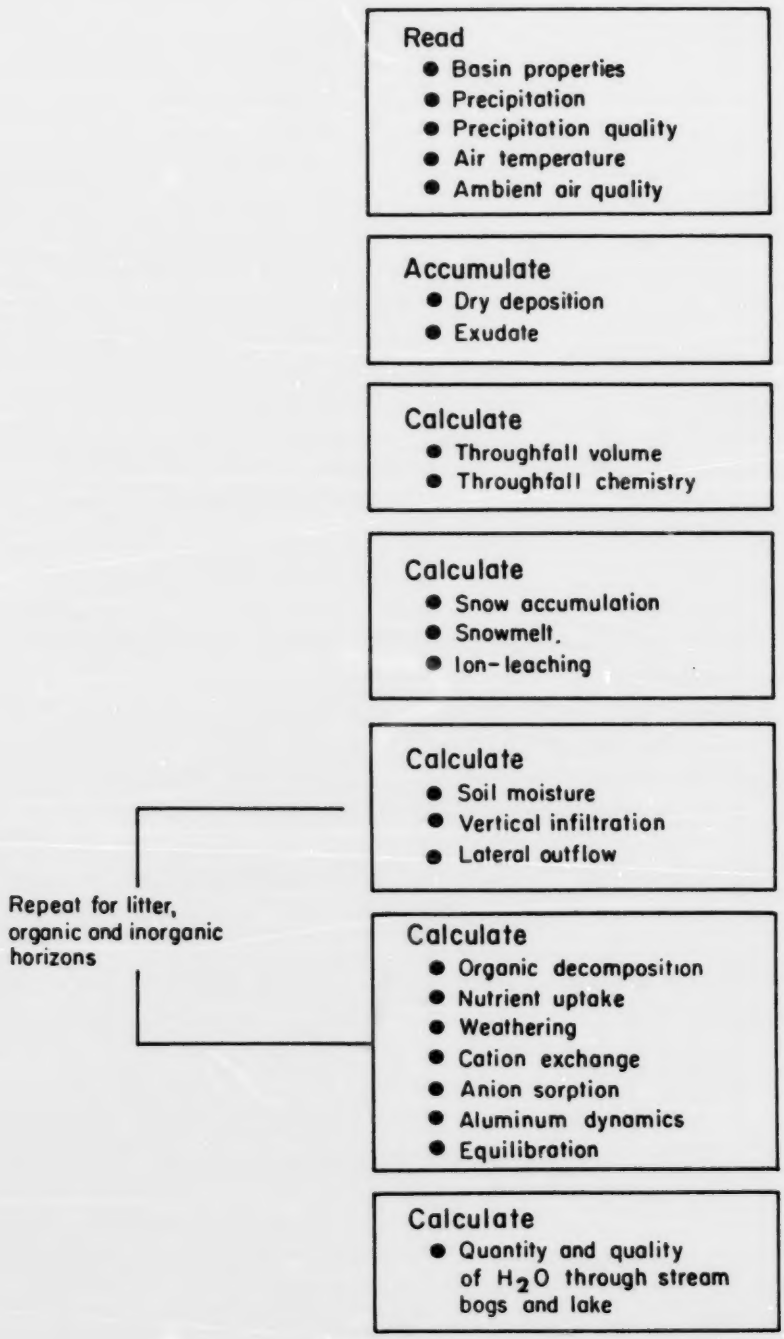

Figure 39. Computational sequence of the ILWAS model. Source: Tetra Tech Inc. (1983b)

to mercury, these problems in Sweden are being exacerbated by acid rain (Jernelov 1973, cited by Brouzes et al. 1977). Some North American studies have similarly found high mercury levels in fish from poorly buffered lakes and streams; Quebec, New Brunswick, Minnesota, New York, and Maine are included in these studies. The mechanism by which acidic deposition might increase the mercury content of fish is not known and certainly the role of groundwater in the mobilization of mercury has not been documented in these studies.

2.9.2 Lead

The toxicity of lead has also been thoroughly studied. Increased concentrations of lead in the human body are associated with learning impairments and central nervous system toxicity. Fuchs and Olson (1979, cited by Sibul and Vallery 1982) found lead levels to be notably high in some domestic water supplies with low pH and alkalinity values. Sharpe and Young of Pennsylvania State University (1982) reported that a Pennsylvanian study showed elevated lead levels in water associated with roof catchment systems. While some of the lead present may be attributable to atmospheric deposition, Sharpe and Young (1982) also attributed increased lead to the corrosion of metal pipes and solder joints in the water supply system. Approximately 16% of the households sampled in one western Pennsylvanian county had lead levels in tap water in excess of the United States Drinking Water Standards. Similar studies conducted in Sweden show elevated metal concentrations in acidic tap water (Table 12 and Figure 40).

2.9.3 Aluminum

Another major concern is the growing presence of aluminum in water. Aluminum, the most common metallic element, comprises about 5% of the earth's crust, but it is almost completely insoluble in neutral or alkaline water. In various areas of northern Europe and in the northeastern United States, an inverse correlation between pH level and Al concentration has been documented for surface waters (Wright et al. 1980). Elevated inorganic aluminum concentrations are potentially toxic to fish at concentrations from approximately 0.1 mg L^{-1} (Baker and Schofield 1982).

As recently as 1974, aluminum was thought to be non-toxic to humans, except for dust particles which contribute to pulmonary problems. Studies by several investigators, particularly those of the Veterans Administration Medical Center in Denver (cited by Maugh 1984), showed that victims of dialysis syndrome had high concentrations of aluminum in muscle and bone tissues and that the syndromes occurred primarily in patients at those dialysis centres where the water supply contained significant concentrations of aluminum. Aluminum may also be associated with various types of dementia, including senile dementia, Alzheimer's disease, and Parkinson's disease.

Guidelines have been established in Canada for aluminum concentrations in water used in agriculture. Water supplies for livestock should contain less than 5.0 mg/L to prevent any adverse effects (Environmental Studies Board 1973, cited by McNeely et al. 1979). Waters used for irrigation should generally be limited to 5.0 mg/L Al although the maximum is set at 20 mg/L for use on fine textured, neutral, or alkaline soils (Environmental Studies Board 1973, cited by McNeely et al. 1979).

Table 12. Heavy metal concentrations in tap water in Sweden.

	pH	Zinc µg/L	Copper µg/L	Lead µg/L	Cadmium µg/L
A[1] Raw water	6.0	9.5	1.2	0.4	0.03
Tap water	9.1	0.2	2.3	0.1	0.01
B[2] Raw water	5.8	1.7	5.4	0.7	0.03
Tap water	6.3	4900	83	3.3	3.4
Limiting values		1000 (T)	50 (T)[3]	50 (H)	5 (H)

1 New alkaline filter

2 Exhausted alkaline filter

3 This figure is a technical limiting value at outlet from waterworks and is not fixed with reference to health (H) aspects. There is no hygienic limiting value for the copper content of drinking water (either in Sweden or any other country).

Source: SNV (1981), in Swedish Ministry of Agriculture (1982)

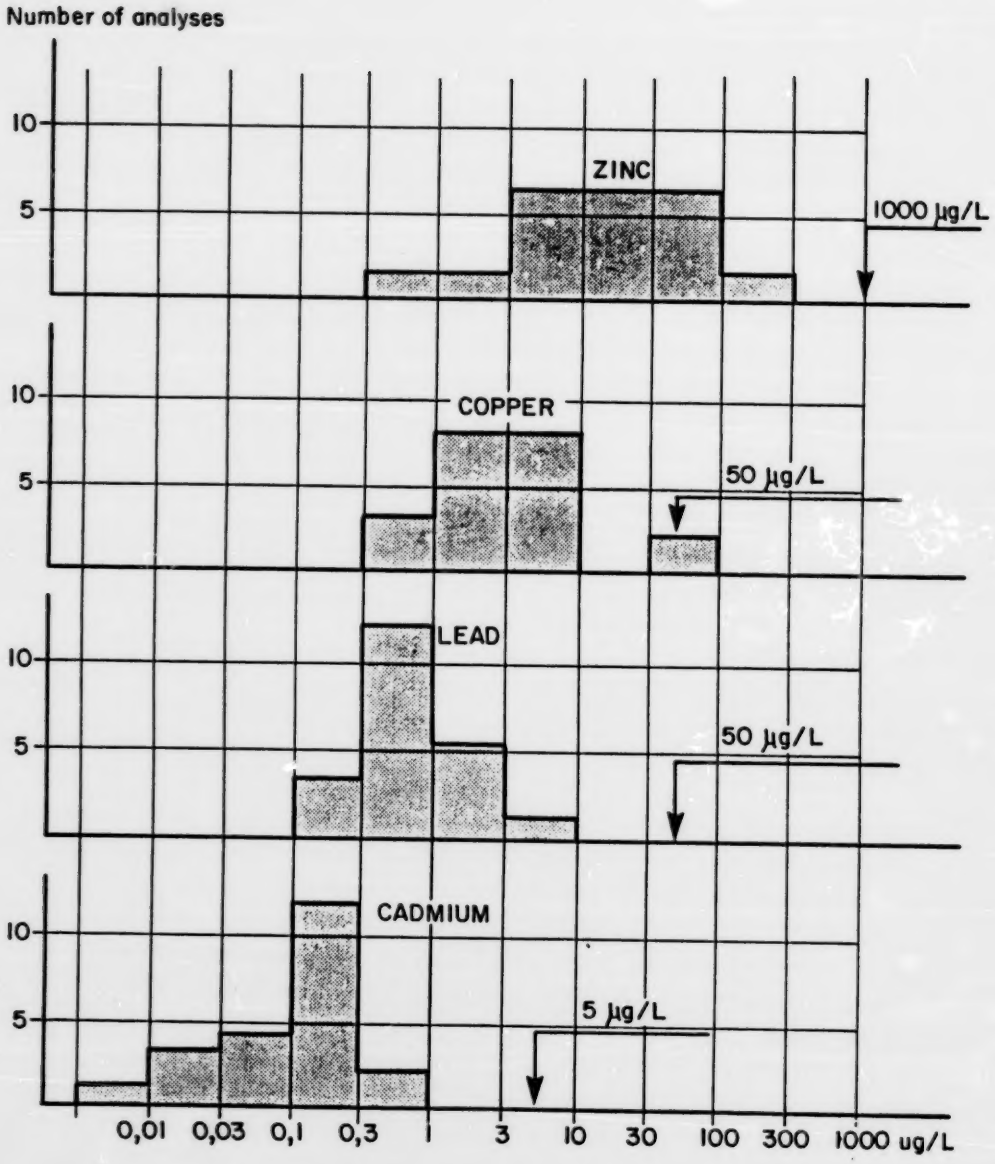

Figure 40. Concentrations of zinc, copper, lead, and cadmium in acid groundwaters in Dalarna and Bohuslan, Sweden. Note that background concentrations are to the left end of the ordinate, and therefore increases in concentration are 10- to 100-fold. Source: Jacks and Kucera (1982)

Industrial operations, especially those using water for steam generation, may find aluminum concentrations troublesome because aluminum can cause scale to form on boiler tubes. A concentration of 0.1 mg/L aluminum has therefore been suggested for good boiler feed water (Great Lakes Water Quality Board 1976, cited by McNeely et al. 1979).

No Canadian guidelines have been established to protect aquatic biota, but a tentative limit of 0-100 mg/L has been proposed (International Joint Commission 1977, cited by McNeely et al. 1979). Elevated levels of aqueous aluminum appear to have deleterious effects on fish in dilute waters (Cronan and Schofield 1979; Schofield and Trojnar 1980, cited by Driscoll et al. 1980). Fish fry are particularly sensitive to hydrolized aluminum (Baker and Schofield 1980).

2.9.4 Copper

In some cases, copper concentrations of >1 mg/L have been shown to cause diarrhea in young children and bad taste in water. In several cases, women's hair has become green coloured after washing in tap water with elevated copper. Concentrations as high as 20 mg/L have been recorded in cold water and 45 mg/L in hot water that has been immobile in pipes overnight. As the concentration of copper increases in domestic water supplies, chinaware and textiles may suffer discoloration. Small amounts of copper (up to 1-2 mg/L) are, as far as we know, not dangerous to the well-being of healthy adults (Holtmeier et al. 1978, cited by Swedish Ministry of Agriculture 1982).

2.9.5 Nitrate

The variation in nitrate content for different waters is great and in many groundwaters, it appears to be unrelated to any geological formation. The nitrate content of the soil, however, is built up from several sources.

Because nitrate may be derived from sewage waste, its presence in water has been considered as evidence of contamination. However, it should be mentioned that such pollution could be expected to add not only nitrate but also chloride to the groundwater. High nitrate, together with high chloride, is thus a more positive indication of sewage effluent or barnyard pollution than nitrate alone.

The maximum concentration of nitrate nitrogen for public water supplies is 10 mg/L (45 mg/L when expressed as nitrate). At higher nitrate levels, young infants (generally less than 4 months old) could die from methomoglobinemia or blue baby disease. Gastric juices of such infants lack sufficient acidity, and nitrate reducing bacteria can grow in their upper intestinal tracts. When they ingest nitrate, the nitrate can then be reduced to nitrite before the nitrate is completely absorbed into the bloodstream. The nitrite reacts with the hemoglobin to form methomoglobin, which is ineffective as an oxygen carrier. This produces anoxemia, symptomized by a greyish or brownish-blue discoloration of the skin, and can lead to death by asphyxia. Older infants and adults can tolerate higher nitrate levels in drinking water and food because their stomach pH is too low for nitrate reducing bacteria. However, nitrate may also play a role in the production of mitrosomines in the stomach, which are known carcinogens (Wolff and Wasserman 1972). This was considered by Hill et al. (1973) as a possible reason for a higher death rate from gastric cancer in a group of people that had a high nitrate level in their drinking water.

Most cases of methomoglobinemia in Europe and the United States have been associated with waters containing more than 11 mg/L of nitrate nitrogen. In the US, 278 cases caused by well water nitrate were reported for the period 1945-1950, resulting in 39 known deaths. The number of reported cases decreased to 40 for the period 1952-1966 and to 10 for the period 1960 to 1969, with no fatalities (National Research Council 1972). Cases of this disease have not been reported in Canada in areas where the drinking water consistently contains less than 10 mg nitrate nitrogen per litre. Where both nitrate and nitrite are present, the total nitrate plus nitrite nitrogen should not exceed 10 mg/L.

The maximum acceptable concentration of nitrite in drinking water, 1.0 mg/L as nitrite nitrogen, is based, as with nitrate, on the relationship between nitrite in water and the incidence of infantile methemoglobinemia. Nitrite is quickly oxidized to nitrate and is, therefore, seldom present in surface waters in significant concentrations. Nitrite may occur in groundwater sources and if chlorenation is practised, it will be oxidized to nitrate.

Similarly to man, livestock are subject to adverse effects when they consume water that contains nitrates. The concentration of nitrate producing deleterious effects varies with the type of animal. A guideline with a reasonable margin of safety for livestock water supplies of 20 mg/L of nitrate plus nitrite has been established (Ontario Ministry of the Environment 1974).

Ammonium nitrogen is undesirable in water for public supplies primarily because of taste and odour. It also reacts with chlorine and increases the amount of chlorine necessary to disinfect the water. For these reasons, the recommended level for ammonium nitrogen in drinking water is 0.5 mg/L. Increased concentrations of dissolved N_2 and N_2O are not detrimental to drinking water.

2.9.6 Sulphate

Moderately high concentrations of sulphate (200-300 mg/L) may be objectionable in water, and magnesium sulphate may be cathartic to humans. Although a laxative effect may be experienced when concentrations range between 150 and 500 mg/L, an objective of less than 150 mg/L for drinking water has been established and concentrations up to 500 mg/L are acceptable for drinking (Department of National Health and Welfare 1979). Waters with concentrations in excess of 500 mg/L may have a more objectionable taste and result in gastro-intestinal irritation and are, therefore, not recommended for human consumption.

Livestock water may contain sulphate concentrations of up to 1000 mg/L and still be considered acceptable (Hart 1974). Concentrations in excess of 250 mg/L may restrict the use of a water by certain industries. A hard scale of calcium sulphate may be formed on pipes, condensers, and boilers. Beverage and ice plants must limit the amount of sulphate in the water they use. Sulphate can corrode concrete.

2.9.7 Ontario Study of Metal Concentrations in Groundwater and Domestic Water Supply Systems

In 1980-82, Ontario Environment carried out a synoptic survey of groundwater quality in the Sudbury-Muskoka-Haliburton area (Sibul and Vallery 1982; Sibul and Reynolds 1982). To obtain an indication of the trace metal content of groundwaters in the Ontario study, one set of samples was taken at random and analysed for the metals shown in Table 13. Another set of samples was taken from four locations in domestic distribution systems to determine the trace metal content due to leaching of metals from household plumbing. In the latter survey, a set of three samples was taken at each location:

1. a sample from the hot water system, with no previous flushing of the system;
2. a sample from the cold water system, with no previous flushing of the system; and
3. a sample from the same cold water system after several minutes of flushing.

With a few exceptions, results indicated generally low background levels of most trace metals (Table 13). Arsenic, cadmium, and chromium were consistently low, while levels of the other metals varied considerably, but all were usually well below the drinking water objectives. Aluminum, copper, and zinc levels in a few samples were noteworthy because the levels were well above those in the majority of samples. The highest copper value of 0.92 mg/L in one sample was just below the drinking water objective of 1.0 mg/L, while copper levels in the other four low-pH samples were considerably less and generally close to background levels.

Zinc levels above 1.0 mg/L were found in two samples although subsequent sampling of flushed cold water at one of these sites had a zinc content of only 0.45 mg/L. The reason for the 2.8 mg/L concentration of zinc in the other sample (pH = 7.2) was not obvious but may have been related to the fact that the sample was obtained from a shallow well equipped with a hard pump used by summer residents only.

The corrosiveness of some of the waters, and the effects of this on the water chemistry of domestic supplies, is indicated by samples 12, 40, 48, and 79 in Table 13. The most notable effects are on the copper concentrations in samples from household taps not flushed prior to the taking of the sample. Except in one sample where the cold water flush/no flush copper concentrations were the same, the highest concentrations in all other samples were in the hot water/no flush samples. These were followed by the cold water/no flush samples, and the lowest concentrations were obtained in the cold water/flush samples. At only one location did the copper values exceed the Drinking Water Objective of 1.0 mg/L (Table 14), although values of 0.92 in sample 48, and 0.88 in sample 12 approached it, and it is conceivable that at these locations the copper concentrations in hot water may exceed the Drinking Water Objective occasionally. The domestic plumbing at all four sample sites was copper, and the high copper levels were probably derived from the plumbing system. It should be noted that the copper objective of 1.0 mg/L is based on taste rather than toxicity and that since the high values were found in the "no flush" samples, copper does not likely present a health hazard.

Table 13. Trace metal analyses of groundwater quality in central Ontario, 1980. Source: Sibul and Vallery (1982)

Sample Number	Location	Date	pH Field/ Lab	Constituents in Milligrams per Litre (mg/L) Aluminum as Al	Arsenic as As	Barium as Ba	Cadmium as Cd	Chromium as Cr	Copper as Cu	Lead as Pb	Zinc as Zn	S.I. at 25°C
Drinking Water Objective			-	-	0.5	1.0	.01	.05	1.0	0.5	5.0	
3(R)	Muskoka Lakes (Medora) C10, L22	16/07/80	5.8/7.1	.30	-	-	-	-	-	-	-	-3.4
6(R)	Muskoka Lakes (Medora) C2, L23	16/07/80	6.4/6.2	.28	-	-	-	-	-	-	-	-3.6
8(R)	Muskoka Lakes (Monck) C13, L29	16/07/80	7.0/7.9	.16	-	-	-	-	-	-	-	-1.4
12	Bracebridge (Macaulay) C7, L7	18/07/80	5.3/6.6	.03	<.001	.04	<.002	.009	.066	<.03	.039	-4.3
12*	Bracebridge (Macaulay) C7, L7	25/11/80	5.5/-	1. <.02	<.001	<.02	<.002	<.02	.88	<.03	.87	-
				2. <.02	<.001	.02	<.002	<.02	<.01	<.03	1.4	-
				3. <.02	<.001	.03	<.002	<.02	<.01	<.03	.13	-
16	Bracebridge (Draper) C2, L5	10/10/80	6.1/-	.26	<.001	.08	<.002	<.02	<.01	<.03	.01	-3.4
27(R)	Bracebridge (Draper) C5, L18	23/07/80	7.2/7.5	<.02	-	-	-	-	-	-	-	-1.3
40*(R)	Dysart C6, L22	25/11/80	6.1/-	1. <.02	<.001	.03	<.002	<.02	2.4	<.03	.36	-
				2. <.02	<.001	.04	<.002	<.02	1.5	<.03	.25	-
				3. <.02	<.001	.04	<.002	<.02	.12	<.03	.21	(-3.7)
48*	Cardiff C20, L25	25/11/80	6.1/-	1. <.02	<.001	.07	<.002	<.02	.92	<.03	.09	-
				2. <.02	<.001	.05	<.002	<.02	.41	<.03	.06	-
				3. <.02	<.001	.06	<.002	<.02	.07	<.03	.03	(-4.1)
64	Huntsville (Chaffey) C10, L17	07/10/80	5.7/5.8	<.02	<.001	.04	<.002	<.02	.28	<.03	.05	-
71(R)	Lake of Bays (Franklin) C14, L20	07/10/80	8.2/8.5	.06	<.001	<.02	<.002	.05	<.01	<.03	.08	-0.5

continued...

Table 13 (Concluded).

Sample Number	Location	Date	pH Field/ Lab	Aluminum as Al	Arsenic as As	Barium as Ba	Cadmium as Cd	Chromium as Cr	Copper as Cu	Lead as Pb	Zinc as Zn	S.I. at 25°C
				Constituents in Milligrams per Litre (mg/L)								
Drinking Water Objective			-	-	0.5	1.0	.01	.05	1.0	0.5	5.0	
79	McClintock C14, L16	15/10/80	5.6/-	.39	.002	.08	.006	<.02	<.01	<.03	.02	-4.3
79*	McClintock C14, L16	25/11/80	5.9/-	1. .20	<.001	.10	<.002	<.02	.37	<.03	.08	-
				2. .31	<.001	.06	<.002	<.02	.13	<.03	.03	-
				3. .32	<.001	.08	<.002	<.02	<.01	<.03	.01	-

NOTES:

* For samples 12, 40, 48, and 79: 1. sample from hot water tap, no flushing
2. sample from cold water tap, no flushing
3. sample from cold water tap after flushing

(R) Rock wells; all others are overburden wells; this distinction is made for purposes of this table only.

S.I. values in brackets were calculated from data obtained from samples taken at a date other than the one shown on this table.

Source: Sibul and Vallery (1982)

Table 14. Maximum acceptable levels in water used for domestic consumption, Health and Welfare Canada.

Parameter	Level
Alkalinity, Total, as $CaCO_3$	≥30, ≤ 500 mg/L
Ammonia, as N	≤0.5 mg/L
Arsenic, as As	≤0.05 mg/L
Bacteria, Fecal Coliform	ND Na/dL
Bacteria, Total Coliform	≤10 Na/dL
Barium, as Ba	≤1.0 mg/L
Boron, as B	≤5.0 mg/L
Cadmium, as Cd	≤0.005 mg/L
Calcium, as Ca	≤200 mg/L
Cesium-137	≤50 Bq/L
Chloride, as Cl	≤250 mg/L
Chromium, as Cr	≤0.05 mg/L
Colour	≤15 TCU
Copper, as Cu	≤1.0 mg/L
Cyanide, as CN	≤0.2 mg/L
Fluoride, as F	≤1.5 mg/L
Hardness, Total, as $CaCO_3$	≤120 mg/L
Iodine-131	≤10 Bq/L
Iron, as Fe	≤0.3 mg/L
Lead, as Pb	≤0.05 mg/L
Magnesium, as Mg	≤150 mg/L
Manganese, as Mn	≤0.05 mg/L
Mercury, as Hg	≤1.0 µg/L
Nitrate + Nitrite, as N	≤10.0 mg/L
Nitrite, as N	≤1.0 mg/L
NTA, as H_3NTA	≤50.0 µg/L
Oil and Grease*	ND mg/L
pH	>6.5, ≤8.5
Phenolic Substances, as Phenol	≤0.002 mg/L
Phosphate, Total Inorganic, as P	≤0.065 mg/L
Phosphate, Total, as P*	<0.100 mg/L
Phosphorus, as P**	≤0.2 mg/L
α-Radiation, Total*	≤0.02 Bq/L
β-Radiation, Total*	≤0.19 Bq/L
Radium-226	≤1.0 Bq/L
Selenium, as Se	≤0.01 mg/L
Silver, as Ag	≤0.05 mg/L
Sodium, as Na**	≤270 mg/L
Strontium-90	≤10 Bq/L
Sulphate, as SO_4	≤500 mg/L
Sulphide, as H_2S	≤0.05 mg/L
Sulfactants, as MBAS	≤0.5 mg/L
Temperature	≤15 °C
Total Dissolved Solids	≤500 mg/L
Trihalomethanes	≤0.35 mg/L
Tritium	≤40,000 Bq/L
Turbidity	≤5 NTU
Uranium, as U	≤20 µg/L
Zinc, as Zn	≤5.0 mg/L

* US Environmental Protection Association
** Australian Water Resources Council
ND = not determined

Although no samples were obtained from systems with lead plumbing, it can be expected that corrosive waters may have similar leaching effects on lead plumbing. Because the lead objective is set in consideration of health effects from long-term consumption, the level of lead in old domestic supplies with lead plumbing might be of concern. Future sampling of water from domestic supplies with lead plumbing will involve the analysis of lead concentrations to provide basic data in this issue.

The only other metal to show somewhat higher levels in the four domestic samples was zinc. All zinc levels were well below the Drinking Water Objective of 5.0 mg/L, with the highest levels generally found in the hot water samples. All of the other metal concentrations were considered representative of background levels in groundwater in the general area.

In reviewing Table 13, it would appear that some groundwaters contain aluminum considerably above the 0.02 mg/L detection limit, with most of the other metal concentrations being generally low and well below the Drinking Water Objectives. The 0.05 mg/L concentration of chromium in sample 71 is notable because it is at the limit of the Drinking Water Objective. However, the reason for this high level is not known.

2.9.8 New York State Study

A study of well water qualities in the Adirondack Mountains of New York State by Fuchs and Olsen (1979, cited by Sibul and Vallery 1982) revealed excessive concentrations of some trace metals in drinking water. The source of these metals was related to leaching from natural bedrock and overburden formations, and to leaching from metal piping in household distribution systems. Copper and lead were found to be notably high in some domestic water supplies with low pH and alkalinity values. Aluminum levels were found to be high in some spring-derived water samples.

2.9.9 Canadian Health Concerns

Testimony given to the Sub-Committee on Acid Rain by Health and Welfare Canada (1981) suggested that the contamination of potable water by toxic metals is probably not a serious problem for most Canadians who obtain water for domestic purposes from a municipal water treatment facility. However, there remains the concern that many Canadians, particularly those who live in rural areas for all or part of the year, are at risk due to the effects of acidified water supplies. Although the technology for treating water on a domestic scale is rapidly improving (i.e., water softeners, activated carbon filters, reverse osmosis), many rural Canadians are drinking water from wells or from similar untreated sources and such waters may contain concentrations of certain chemicals such as heavy metals that are harmful. Although the number of people at risk may be small in relation to the total Canadian population, the concern of individual users or groups of users cannot be ignored. The Province of Prince Edward Island, which is entirely dependent on groundwater for potable and process water supplies is notably concerned about the quality of groundwater on the Island.

From a toxicological point of view, the metal concentrations observed in Canada are, so far, within acceptable limits, but the risk is that under certain circumstances (high dose deposition or desorption) there may arise heavy metal concentrations in water supplies that constitute a health hazard.

3. RESOURCE INVENTORY OF ALBERTA

3.1 BEDROCK GEOLOGY

The bedrock geology of Alberta is shown on Plate 1, 1:1,000,000 scale Provincial map after Green (1972). The Alberta geology is discussed in detail below.

3.1.1 Source of Data

The bedrock geology of Alberta has been examined for various map sheets, regions, and time periods by numerous individuals. Most of the published work on bedrock geology has been completed either by the Geologic Survey of Canada or the Alberta Research Council. The Alberta Energy Resources Conservation Board has also produced numerous publications generally relevant to coal or hydrocarbon development.

As the purpose of the present study is to inventory the resources of Alberta, the main data source was the Geological Map of Alberta (Green 1972).

3.1.2 Overview of Geology of Alberta

The oldest bedrock in Alberta is the Precambrian age crystalline rock of the Canadian Shield in the northeastern corner of the province. This rock forms the "basement" under the rest of Alberta, dipping gently to the west at a rate of 1 km per 125 km. The Precambrian Shield is an erosional remnant of Precambrian mountains which existed to the north of Alberta (Yellowknife area) and to the east (from Lake Superior to Montana). Western Canada and Alberta, therefore, were under the Pacific Ocean in what was the start of the Western Canadian Sedimentary Basin.

Since Precambrian times, the Pacific Ocean has advanced and retreated with various uplifts and with changes in sea levels. Bedrock sediments in Alberta, therefore, are a reflection of the various marine and non-marine depositional environments since Precambrian times.

Generally, the bedrock geology of Alberta can be discussed for the three main Physiographic Regions of the province: the Canadian Shield, the Rocky Mountain Cordillera, and the Western Plains.

The Canadian Shield in Alberta is present in the northeastern corner of the province. In this area, Pleistocene glaciation has scoured the bedrock surface, exposing the Precambrian basement rock. Along the western edge of the Shield, in the Athabasca Delta area, Devonian age carbonates and evaporites are the uppermost bedrock strata.

The Rocky Mountain Cordillera region was uplifted during the Tertiary Period. The Rocky Mountains are the result of upthrusting, so that older bedrock strata overlie younger rocks. As such, rocks of the Proterozoic, Paleozoic, Mesozoic, and Cenozoic Eras are exposed in the mountain region of the province.

Most of the province is contained within the Western Plains Physiographic Region. Bedrock underlying this area consists predominantly of Cretaceous and Tertiary age sediments, both non-marine and marine in origin. The exception to this is the area of Devonian strata bordering the Canadian Shield in northeastern Alberta.

3.1.3 Characteristics of Bedrock

3.1.3.1 Lithology and mineralogy. As mentioned previously, the uppermost bedrock for a majority of the province comprises Cretaceous and Tertiary age sediments. In the northern portion of the province, north of Lesser Slave Lake, the sediments are mostly of Cretaceous and lower Cretaceous age and are marine in origin. Shale, dark grey in colour, is the dominant lithology with formations such as the Shaftesbury, Loon River, Smokey Group, and La Biche. An exception to this is the Dunvegan Formation in northwestern Alberta which is comprised of deltaic sandstones, siltstones, and marine shales.

In the southern half of the province, the uppermost bedrock strata are predominantly Upper Cretaceous to Tertiary age and non-marine in origin, consisting of interbedded shales, siltstones, sandstones with occasional coal seams, and Bentonite beds. The Bearspaw Formation of southeastern Alberta, however, is a marine unit consisting predominantly of shales.

The Cretaceous and Tertiary sandstones of Alberta are typically very fine to fine-grained and poorly consolidated (Carrigy and Mellon 1964).

The shales and sandstones of the southern portion of the Interior Plains Region are high in montmorillonite clay. In most cases, montmorillonite comprises more than 50% of the clay fraction of the Cretaceous-Tertiary Alberta shales followed by illite and chlorite (Pawluk and Bayrock 1969). Kaolinite comprises a small percentage of shale in the plains region with the exception of the Whitemud Formation in the Cypress Hills where kaolinite is relatively abundant. Bentonite layers in the Cretaceous-Tertiary strata contain over 95% mortmorillonite clays. In the northern portion of the province, the dominant clay mineral in shales is illite.

In Cretaceous-Tertiary sandstones of the Alberta plains, Kaolinite is the most widely distributed clay mineral cement (Carrigy and Mellon 1964) both in marine and non-marine deposits. Montmorillonite and glauconite are also both common, particularly in association with detrital fragments usually in sandstones rich in volcanic detritus. The Cretaceous-Tertiary sandstones have a high proportion of unstable igneous (volcanic) detritus.

The mineral fraction is comprised of siliceous, micaceous, and volcanic detritus derived from a metasedimentary source area to the west and an authigenic chemically precipitated fraction (siderite, calcite, clay minerals, and zeolites).

The Canadian Shield in the northeastern corner of Alberta is comprised of Precambrian crystalline rocks (granitics) and Precambrian sedimentary and metasedimentary rocks.

In the Cordilleran region of Alberta, the litholigies are extremely complex. The Frontal Range of the Rocky Mountains consists of predominantly Paleozic carbonate and shales that thrust over the younger Mesozoic sediments. The main range of the Rockies is mostly comprised of older strata - Precambrian and Cambrian sandstones, shales, and limestones. The foothill region bordering the Rocky Mountains characteristically consists of long northwesterly trending ridges with steep-sided valleys of folded and faulted Mesozoic sandstones and shales with occasional limestones. The province's only volcanic rocks outcrop in the Rocky Mountains of the Crowsnest area in southern Alberta.

3.1.3.2 Chemistry. Pawluk and Bayrock (1969), in their study of Alberta tills, correlated most of their findings to the bedrock underlying the glacial deposits. They analysed tills for calcium oxide and the elements iron, boron, cobalt, copper, zinc, and molybdenum.

Calcium oxide directly reflects calcitic and dolomitic material from the Paleozoic strata encountered in the Cordilleran region and along the Shield.

The iron content in Alberta bedrock is variable. Higher iron contents are typical of pyritic sediments of the Cretaceous Smokey Group in northwestern Alberta and in iron-rich, oolitic material of the Bad Heart Formation of the Clear Hills area. In southern and central Alberta, iron is present to a limited extent in ironstone nodules of the non-marine Cretaceous-Tertiary strata.

Zinc values of Alberta bedrock also vary regionally. Lowest values are found in northeastern Alberta in the area of Devonian carbonates and in the Cordilleran region (<50 ppm). Highest values are encountered in Shaftesbury shales in northwestern Alberta (96-216 ppm).

Copper values of Alberta bedrock show a distribution similar to zinc and iron. Low values (<20 ppm) are found in the Shield and Cordilleran regions, mid values in south and central Alberta Cretaceous-Tertiary rocks, and high values (27 to 48 ppm) in the Clear Hills area (Shaftesbury Formation).

Manganese in bedrock has not been studied. However, ironstone nodules abundant in south and central Alberta Cretaceous-Tertiary sediments contain manganese oxides. Tills in this region are uniform in manganese content (0.030% to 0.045%) with lower values found elsewhere.

Contents of molybdenum, cobalt, and boron in Alberta bedrock have not been studied. The boron distribution in tills would indicate that it is highest in areas of marine shales in the northern portion of the province.

Salt content in soils is related to groundwater discharge and not to bedrock (Pawluk and Bayrock 1969).

3.2 SURFICIAL GEOLOGY

The surficial geology of Alberta has been completed for this study at a scale of 1:1,000,000 (Plate 2) using existing published and unpublished available reports and maps.

3.2.1 Sources of Data

The main sources of data used in constructing the Alberta surficial geology map (Plate 2) were the surficial geology maps and reports by the Geological Survey of Canada and the Alberta Research Council. The common scale of this mapping is 1:250,000; however, various other scales were used for different areas of the province.

Surficial geology mapping has not been completed for all areas of the province; therefore, other sources of data were used for the unmapped areas. These included surficial geological information from the Exploratory Soil Survey Map Series and Reconnaissance Soil Survey Map Series produced by the Alberta Research Council. The Exploratory Soil Survey mapping is completed at relatively small scales (1:633,600 to 1:760,320) for the northern portion of the province. Surficial geology information in these reports, if present, is usually very generalized.

The Reconnaissance Soil Survey Map Series has been completed for most of the farming areas of Alberta. Mapping scale varies between 1:125,000 and 1:250,000. Surficial geology information is incorporated into these soils maps and is therefore quite detailed. A certain amount of interpretation, however, is necessary in making the mapping consistent with the surficial geology terminology of the Geological Survey of Canada and the Alberta Research Council.

Data gaps in the northern portion of the province were filled in by using the Special Geomorphic Landform Maps (scale: 1:63,360) completed by the Lands Directorate of Environment Canada, and by Alberta Energy and Natural Resources.

The above sources of surficial geology information gave complete coverage of the province with the exception of the Vermilion Map Sheep (NTS 37E) and some small areas along the foothills west of Calgary. Information on these areas was kindly provided by I. Shetsen and C. Mougest of the Alberta Research Council, who are currently preparing maps of the surficial geology of southern Alberta and Vermilion Map Sheet, respectively.

Figure 41 is a map showing the sources of data for the various areas. Individual references used are detailed in Section 7 at the end of this report.

3.2.2 Surficial Geology Map Legend

The 1:1,000,000 surficial geology map (Plate 2) was assembled from various data sources at various scales, but mostly from large scale mapping. As a result, the legend and mapping used here has greatly simplified and generalized the previous works. The legend uses only the main genetic landform type with no qualifiers. Therefore, the legend consists of Organics (O), Alluvial (A), Colluvial (C), Eolian (E), Lacustrine (L), Glaciofluvial (G), Morainal (M), and Bedrock (R).

Most of the interpretation for the above units is straight-forward; however, one interpretation made for this study should be noted. Course-grained glaciolacustrine deposits (silt, sand, gravel) have been included on the map under the Glaciofluvial classification, thereby permitting recognition of the areas of the province with coarse-grained material and separating them from the fine-grained lithologic types. We feel that this interpretation is necessary in assessing the capacity of the landform to buffer acidic deposition.

Interpretation during mapping was also necessary in generalizing or grouping areas of complex surficial geology in transferring from the large scale maps to the small scale (1:1,000,000) sheet. Small areas of a second (or third) genetic type in a large area of, for example, moraine, were ignored in our mapping unless the secondary areas made up a sizeable fraction of the total area. In these cases, a complex would be used (see Map Sheet Legend, Plate 2). A good example of this is in the northern portion of the province where organics are abundant. Unless the organics formed the predominant type in an area, no reference was made to them.

A great deal of interpretation was also necessary along the borders of map sheets where different geologists may have had different mapping interpretations. In most cases, the more recent mapping was assumed to be correct in our interpretation.

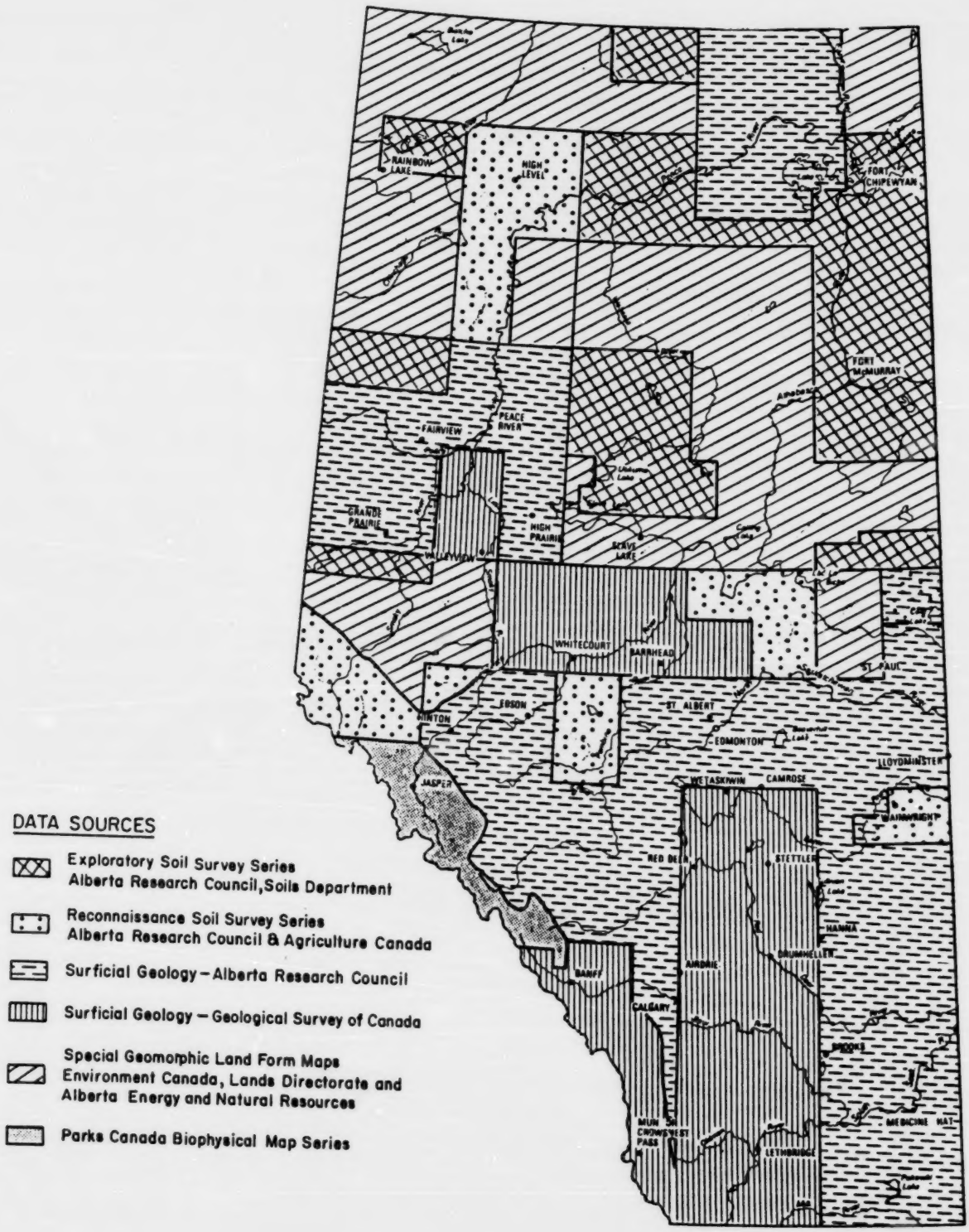

Figure 41. Surficial geology of Alberta data sources.

3.2.3 Overview of Surficial Geology of Alberta

Prior to glaciation in late Tertiary and early Pleistocene time, the Alberta landscape was similar in appearance to the present. Surficial materials, however, did not include glacial deposits and as such, were generally thin except in river valleys of that time. Extensive erosion of the Tertiary and Cretaceous bedrock sediments by fluvial and mass wasting processes resulted in deposition of the Saskatchewan Sands and Gravel. These deposits are most prevalent in the bottom of buried bedrock valleys which represent the preglacial drainage system of the province (Figure 42).

Pleistocene glaciation in Alberta significantly changed the landscape and drainage system. In North America, there were four major advances of ice sheets and subsequent interglacial periods of ice retreat. In Alberta, the first three glacial advances may have only reached or crossed Alberta's eastern border. The last ice advance, however, the Wisconsin Glaciation approximately 35,000 years ago, covered all of Alberta with the exception of the higher mountain peaks, the Cypress Hills, and small portions of the Porcupine Hills.

The regional direction of the last glacial advance has been shown by Gravenor and Bayrock (1961) to be from northeastern Alberta to the southwest (Figure 43). The continental glaciation near the Foothills was met by the Cordilleran ice sheets moving from the west and the ice direction shifted to the southeast, south of Edmonton. Retreat of the Wisconsin Glaciation began approximately 12,000 years ago. During glacial retreat the morainal, glaciolacustrine, and glaciofluvial deposits were left behind. Since glaciation, these deposits have been reworked by wind (eolian deposits), rivers (alluvial deposits), and mass wasting (colluvium). In addition, infilling of depressional areas by recent lake deposits and organics has occurred. Organic deposits are particularly significant in the northern portion of the province.

3.2.3.1 Distribution of surficial deposits. By far the most abundant surficial deposit in Alberta is glacial till occurring in morainal landforms throughout the province. Till deposits comprise approximately 70 percent of the province's surficial deposits. Tills vary in thickness from less that 3 m in areas of ground moraine (the most common landform) to more than 30 m in buried preglacial valleys and areas of hummocky moraine.

Moraine landforms are most common in the southern portion of the province where the topography at the time of glacial retreat allowed for quick runoff without significant glacial lake ponding. North of Edmonton, the drainage system was to the northeast, the same direction as the glacial retreat. As a result, the retreating glaciers formed ice dams on the major drainage systems and huge glacial lakes resulted. Glaciolacustrine deposits, therefore, cover a large portion of northern and northwestern Alberta.

With drainage to the east in southern Alberta and to the northeast in northern Alberta, glaciofluvial (glacial runoff) deposits are most abundant in the eastern portion of the province. In southern Alberta, the glacial lakes were small and their sediments are more deltaic in nature and are therefore coarse-grained. As outlined earlier, coarse-grained lake deposits have been included with the glaciofluvial sediments in the attached map (Plate 2).

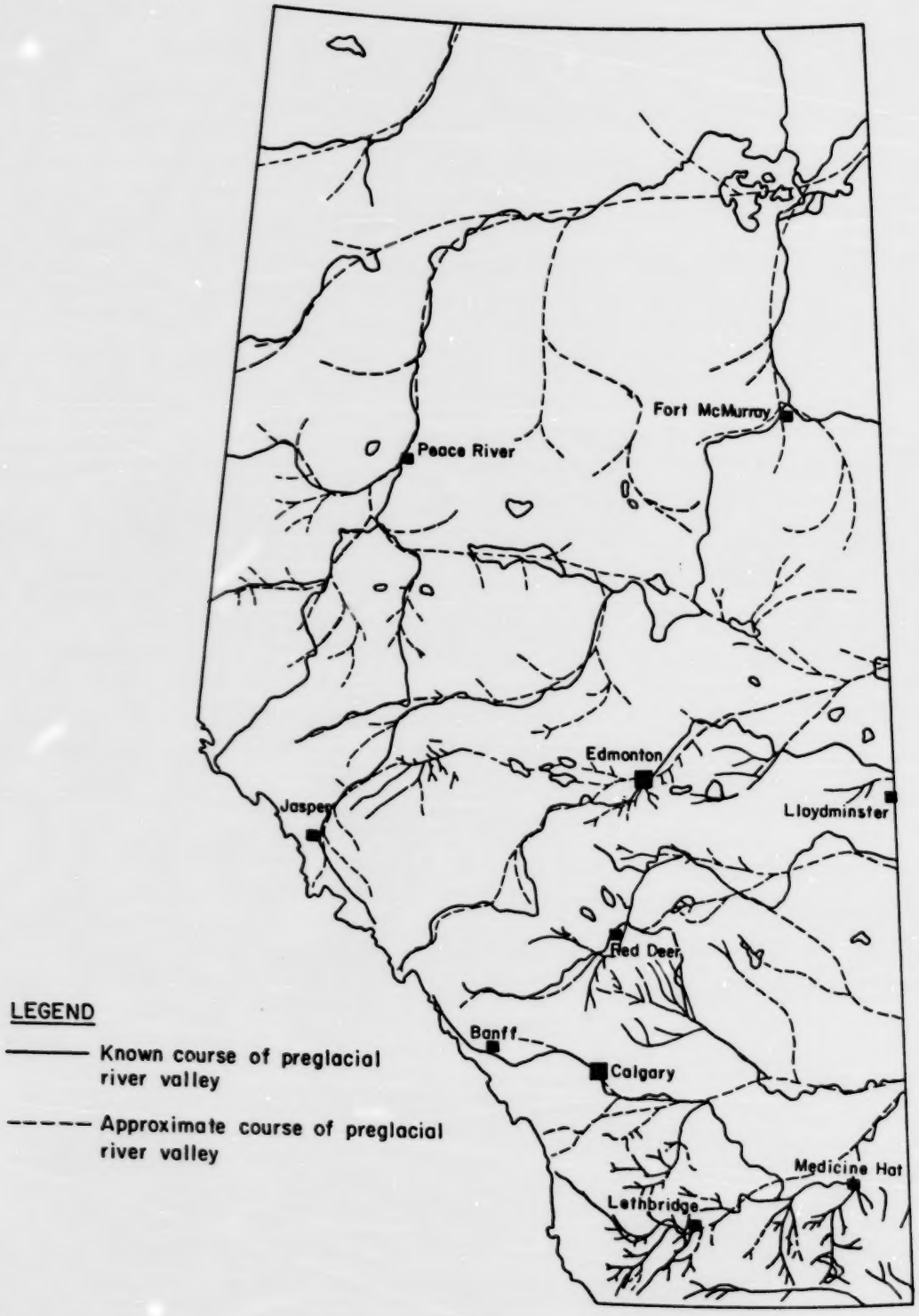

Figure 42. Preglacial river valleys of Alberta. Source: Hardy (1967)

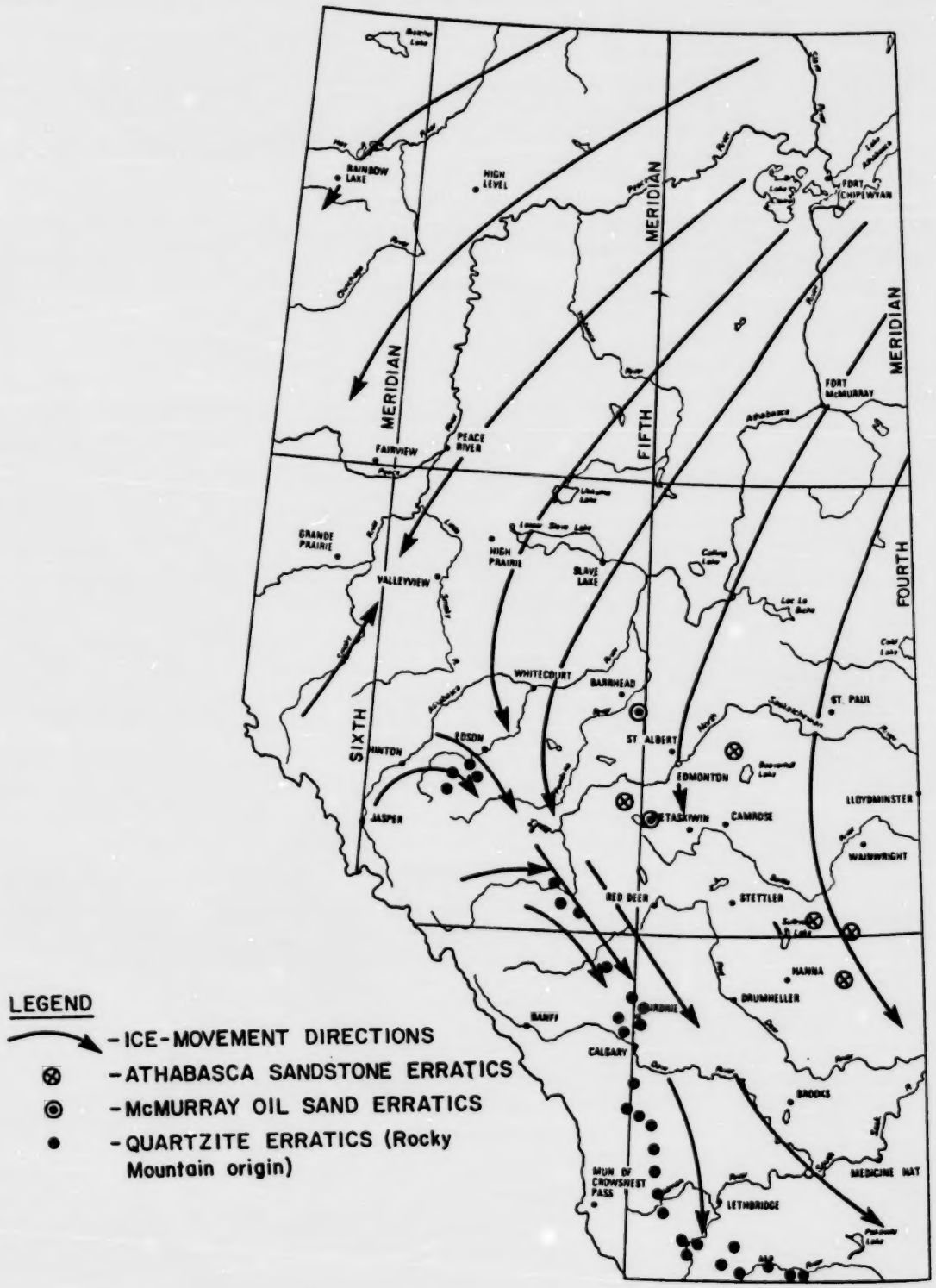

Figure 43. Generalized ice-advance directions in Alberta.

Eolian deposits occur throughout the province in areas where silt and sand occur. The largest areas of eolian deposits occur in the eastern part of the province associated with the glaciofluvial landforms.

Recent alluvial deposits occur in the numerous river and stream valleys of the present day drainage systems. As downcutting of the modern day rivers has in many areas been significant, the steep valley walls have been subjected to mass wasting processes resulting in colluvium. At the small scale of mapping, alluvial and colluvial deposits are often grouped together as a complex.

Colluvium is also present in the unglaciated areas of the province, Cypress Hills, and the Cordilleran region. In the latter region, two groupings are common on the surficial map - the high alpine areas are grouped as bedrock and colluvium, and the subalpine areas as colluvium and morainal deposits.

Organic deposits have infilled depressional areas throughout Alberta. However, south of Edmonton these deposits are generally thin and have not been outlined. In the northern half of the province, organics are a significant surficial material. Further to the north, organics become more and more prevalent.

3.2.4 Characterization of Surficial Deposits

3.2.4.1 Till. Till, being the dominant surficial deposit, has been the subject of numerous studies. In Alberta, tills have been examined by Gravenor and Bayrock (1961), Pawluk (1961), Bayrock (1962), Pawluk and Bayrock (1969), and Twardy et al. (1973). In addition, studies of Alberta tills have been included in numerous regional studies on glacial tills. The main reference used in this study is that of Pawluk and Bayrock (1969).

Texture of tills in Alberta closely reflects the composition of the underlying bedrock strata because the bulk of till deposits is comprised of locally derived material. Tills in northeastern Alberta, adjacent to the Shield, have a high sand content (60% to 70%). Tills in northwestern Alberta have high clay contents, occasionally exceeding 70%, due to their derivation from the Cretaceous marine shales of that area. Low clay contents (10% to 20%) occur in the Cypress Hills area as well as in northeastern Alberta as explained above. Cypress Hills tills, however, tend to be higher in silt content than those from northeastern Alberta. Coarse-grained tills are also common along the Cordilleran region. These latter tills are noted for being extremely stony.

In central and southern Alberta, tills typically fall into the heavy loam, clay loam, and sandy clay loam textural classes. In northern Alberta, tills fall into the clay loam class in the east with fineness increasing westwards to the Clear Hills area, which is characterized by tills in the heavy clay class.

The main clay mineral in Alberta tills is a reflection of the underlying bedrock. Montmorillonite content ranges from 20% to 70% with lower values found in the northern regions where the marine shales are illite-rich rather than montmorillonite-rich. Montmorillonite content increases in a southerly direction.

Illite content, therefore, is the inverse of montmorillonite with higher concentrations in tills in northern Alberta and lower amounts to the south. Concentrations of kaolinite, chlorite, and fine-grained quartz comprise only a limited fraction of Alberta tills.

The sand fraction of Alberta tills is largely comprised of the Cretaceous and Tertiary bedrock locally underlying the till. Continental glaciation advanced from the northeast and a small percentage of the mineral content of the tills is derived from the Canadian Shield. This amount increases closer to the Shield. In a westward direction, minerals and rocks derived from the Cordilleran region become more abundant.

Carbonate content in Alberta tills is generally low. However, carbonate content increases towards the mountains and the Shield, reflecting the two carbonate bedrock source areas in Alberta. Very low carbonate contents are typical of tills in and adjacent to the upland-plain remnants of Alberta, such as the Clear Hills, Birch Mountains, Cypress Hills, Hand Hills, Neutral Hills, and Swan Hills.

Carbonate content of tills is highly correlated to pH values. The lowest carbonate contents, which occur in the Clear Hills region, have the lowest pH values (4.0 to 6.5). The higher pH values in Alberta (7.5 to 8.5) occur where the tills are derived from carbonate bedrock such as in the Rocky Mountains and in northeastern Alberta.

The permeability of tills has been examined by Freeze and Cherry (1979) and is known to range from 10^{-3} cm/s to 10^{-10} cm/s depending on textural differences and, most importantly, on fracturing. Non-fractured tills generally have permeabilities in the range of 10^{-5} cm/s to 10^{-10} cm/s.

Pawluk and Bayrock (1969) also examined metal content of Alberta tills. The contents of iron, zinc, copper, and boron in Alberta tills are directly correlated to the underlying bedrock described in Section 3.1.3.

Iron values in tills range from 2% to 4%. Iron concentrations increase to the northwest due to the influence of pyrite-bearing and iron-rich bedrock of the Cretaceous Smokey Group and Bad Heart Formation in the northwest. Lowest concentrations of iron occur in the northeast and southwest portions of the province which are underlain by carbonates.

Zinc concentrations in till range from less than 50 ppm to over 200 ppm. Lowest values occur in the areas underlain by carbonates (northeast and southwest portions of Alberta), and highest values in the areas of the Shaftesbury Formation in northwestern Alberta. Zinc values in southern and central Alberta generally range from 50 to 70 ppm.

The distribution of copper concentrations in Alberta tills is similar to that of zinc and iron. Concentrations range from 5 to 40 ppm. Areas underlain by carbonates or Precambrian rocks have the lowest concentrations (<20 ppm). Southern and central Alberta tills have average copper values in the range of 20 to 25 ppm. Highest copper values occur in the northeast, associated with the Bad Heart Formation and the Smokey Group pyritic shales.

Boron in tills appears to be associated with the clay content. The higher the clay content is, the greater are the concentrations of boron. Values in Alberta tills range from 13 to 70 ppm. Lowest values occur in the southeast and northeast portions of the province where sandier tills occur. Highest values are in the northwest and are associated with heavy clay tills.

Manganese in tills of Alberta varies from 0.008% to 0.055%. Manganese values generally decrease to the north. Manganese oxides which occur in the ironstone nodules in southern Alberta, non-marine bedrock are believed to be the reason for the higher concentrations in the south.

Molybdenum content of Alberta tills is less than 1 ppm throughout most of Alberta. North of Slave Lake, concentrations range up to 3 ppm.

Cobalt concentrations in till are uniform for Alberta and vary locally from 2 to 11 ppm.

Concentrations of water soluble salts in Alberta tills range from 0 to 50 meq g^{-1} with the higher values coinciding with the Solonetzic soils of the province. Salt concentrations in tills, therefore, are considered a result of local hydrogeology and are not bedrock-controlled. In the northern portion of the province, the principal salt is generally magnesium sulphate. In southern and central Alberta, sodium sulphate is the dominant salt precipitate (Pawluk and Bayrock 1969).

3.2.4.2 Lacustrine deposits. Lacustrine deposits are the second most common surficial deposit in Alberta after till. For the purpose of this study, glacial lake sediments and recent lake deposits are grouped together as lacustrine deposits. Glacial lake sediments are particularly important north of Edmonton where the regional drainage promoted establishment of large glacial lakes during the recession of glaciation. Lithologically, glaciolacustrine deposits are typically clay and silt in composition often with interbedding referred to as varves (seasonal deposits alternating fine, light coloured material in winter and slightly coarser, dark, organic rich material in summer).

In southern and eastern Alberta where glacial lakes were relatively small in area and had a short life, sand and silt-sized materials are more common. In this study, sandy glaciolacustrine deposits are included with the glaciofluvial materials for discussion purposes.

From Edmonton north and northwest, clay is the dominant material in lacustrine sediments. To the northeast, towards the Shield, coarser-grained material becomes more dominant.

Although lake sediments are generally fine-grained, in northern Alberta ice rafting of gravel and boulder sized material was common. Glacial lake sediments in these areas, therefore, often contain numerous stones and as a result, are often interpreted as tills. Many of the so-called lacustro-tills of northern Alberta are, in fact, glacio-lacustrine in origin, exhibiting a certain stoniness due to ice rafting.

Sediments in Alberta glacial lakes are a result partly of direct glacial runoff and partly of deposition from the eastward running river systems of the time. As a result, the mineralogy of glaciolacustrine deposits is derived partly from local sources and partly from western sources.

Clay mineralogy is similar to that of tills with montmorillonite predominating in southern Alberta and illite in northern Alberta.

Few studies have been completed in glaciolacustrine deposits in Alberta. Therefore, information is unavailable on characteristics.

Properties and characteristics of glaciolacustrine deposits in Alberta should be similar to those of till; however, regional differences are expected to be more subtle. Carbonate contents are anticipated to be fairly consistent throughout Alberta, due to eastward transport of carbonates by the major river systems flowing from the mountains.

In the Edmonton area, lacustrine deposits are comprised predominantly of clay with some silt and a trace of sand. They are moderately calcareous and have low salinities except in groundwater discharge areas. The dominant clay mineral is montmorillonite and, as a result, the materials range from low to high plasticity.

Lacustrine deposits in the Peace River area are typically a clay (illite predominating), weakly to moderately calcareous, and weakly saline.

Recent lake deposits in Alberta are limited in extent. Lithologically, they are similar to glacial lake sediments except for their high organic content.

3.2.4.3 Glaciofluvial deposits. Glaciofluvial deposits are scattered throughout the province, generally covering relatively small areas. The largest areas of glaciofluvial sediments are in the northeastern portion of the province in the Lake Claire, Lake Athabasca region. Significant deposits are also found in east central Alberta associated with deltaic deposition in glacial lakes.

Depositional environments, and accordingly morphology and characteristics of glaciofluvial sediments, are highly variable. Glaciofluvial materials include fluvial deposits present as flood plains, terraces, and outwash plains along meltwater courses, deltaic deposits in glacial lakes, and ice contact fluvial sediments such as eskers and kames. Glaciofluvial material, therefore, is highly variable, but generally coarse-grained (fine sand to gravel sizes), stratified, and well sorted. Ice contact glaciofluvial deposits, however, are often poorly sorted and have textures ranging from clay till to gravel sizes.

The outwash and deltaic deposits common in the eastern and northeastern portions of the province are typically comprised of silts and sand. Since glacial retreat, these deposits have been particularly prone to reworking by wind. Most of the province's eolian deposits are developed on glaciofluvial outwash plains and deltas.

Due to the great variety of glaciofluvial deposits, little work has been completed on their characterization. Most of the information available is the result of studies completed for industrial material exploration and development. In this regard, studies have been conducted in the vicinities of the major population centres and/or development areas such as Edmonton, Red Deer, Calgary, Fort McMurray, Grande Prairie, Athabasca, Cold Lake, and Lethbridge.

The dominant rock type in the gravel size fraction of most of the glaciofluvial deposits examined is quartzite. The minor constituents, however, vary regionally and even locally within a given deposit.

In the northeastern portion of the province, granitics and carbonates make up a significant portion of the gravel sized fraction due to glacial transport of these materials from the Shield area. Also, closer to the Rocky Mountain areas, carbonates become more abundant. In the Canmore Corridor area (Edwards 1979) carbonates are the most abundant rock type, comprising over 60% of the outwash gravel deposit with sandstones, quartzites, shale, and granitics forming the remaining 40%.

In the glaciofluvial sand deposits of Alberta, silicas, mainly quartz, are the most abundant mineral type (60 to 90%) even near the Rocky Mountains. Carbonates form only a small percentage of the sand content in outwash deposits because with extended transport, carbonates tend to weather and pulverize. Granitics, heavy minerals, and mica generally comprise the remaining fraction of outwash sands.

3.2.4.4 Eolian deposits. Eolian deposits in Alberta are scattered throughout the province, developed on glaciofluvial sediments and coarse-grained lacustrine deposits. The biggest areas of eolian material in Alberta occur in the east central region and in the northeastern portion of the province.

Texturally, eolian deposits consist of fine to medium-grained sand and silt. The grain size distribution varies considerably within a deposit relative to the mechanics of wind deposition. In addition, as the deposits are a result of reworking of other deposits (glaciofluvial and lacustrine), the grain size is also a function of the source material.

The mineral composition of eolian materials has been examined for only a few sites in relation to use of the deposits for industrial purposes. Regional studies have not been completed. In fact, information is not available for the majority of dune areas.

Holter (1972b), in an examination of sand dunes in the Medicine Hat area, found the sand to be comprised predominantly of quartz (82% to 88%) with feldspar, mica, and other minerals constituting the remainder. Chemically, the Medicine Hat sands are comprised of 84% to 89% silica, 5% to 7% aluminum (a function of the feldspar and clay content), and 0.7% to 1.3% iron oxide.

In a study of dune sand in the Red Deer area (Holter 1972a), very similar results were obtained. Quartz accounts for 86% to 93% of the mineral grains, feldspar for 3% to 7%, with mica and other minerals comprising the remainder. Chemically, silica comprises 73% to 87% of the sand, aluminum 6% to 9%, and iron oxide 1.2% to 1.7%.

Eolian deposits generally have little, if any, carbonate content.

Permeabilities of eolian deposits have not been studied in Alberta. Freeze and Cherry (1979), however, indicated that for the grain size distribution of eolian materials c(i.e., silty sand to clean sand)c hydraulic conductivities ofc 10^{-7} cm/s to 1.0 cm/s can be anticipated.

3.2.4.5 Alluvial deposits. Recent alluvial deposits occur along all the present day Alberta rivers and streams. As with the glaciofluvial sediments, alluvial deposits have been examined in the various population and industrial development areas of the province as sources of granular borrow material. Shaw and Kellerhals (1982), however, have completed a regional study of alluvial deposits of Alberta's major rivers.

Texture of alluvial deposits is a function of the distance from the source, the Rocky Mountains. In this regard, Alberta's rivers can each be divided into three reaches: a mountain reach in which there is a tendency for an increase in grain size downstream; a central gravel reach in which grain size decreases with distance downstream; and a lower reach in which only sand sizes occur.

Mineralogy of Alberta alluvial deposits is dependent on the local bedrock and surficial geology as well as on distance from the Rocky Mountains. In the Cordilleran region, alluvial gravels are comprised predominantly of carbonates, with quartzites being the second most abundant rock type. Secondary rock types include shale, sandstone, metamorphics, volcanics, and igneous rocks. Granitics derived from the Shield are absent because the Laurentide (Continental) ice sheet did not reach the mountain areas.

In the middle reaches of Alberta rivers, quartzites become more abundant and carbonates much less so. The further east from the source the higher the quartzite percentage and the lower the carbonate content. Also, granitics from the Canadian Shield become more abundant.

In the third reach, gravel sizes do not occur; only sands are deposited. Lithologically, quartzites are the predominant rock type. Granitics are relatively abundant particularly to the east and northeast.

Permeability of alluvial deposits is a function of the grain size distribution and sorting. In the Cordilleran region, alluvial sediments tend to be comprised of very coarse, clean gravels. Hydraulic conductivities, therefore, are very high, at 1.0 cm/s or better. In slower reaches of rivers on the prairies, sediments tend to be comprised of sand with a significant fine content. Hydraulic conductivities for dirty sands from Freeze and Cherry (1979) are in the order of 10^{-5} to 10^{-3} cm/s. Alluvial deposits, therefore, can have hydraulic conductivities ranging from 10^{-5} to more than 10^{2} cm/s depending on the local (historic and present) stream morphology.

3.2.4.6 Colluvium. Colluvium is the result of mass wasting processes on all bedrock and surficial deposits. Colluvial deposits occur throughout Alberta, generally on the steeper slopes such as along river banks. The largest areas of colluvium occur in the mountain region of the province where colluvium is the result of mass wasting of bedrock. Unglaciated areas of the province such as the Cypress Hills also contain significant areas of colluvium.

Colluvium forms from reworking of bedrock and surficial material and, therefore, textural, mineralogical, physical, and chemical characteristics are highly variable, generally reflecting the characteristics of the parent material.

3.2.4.7 Organics. Since Pleistocene times, poorly drained depressional areas of the province, particularly in northern Alberta, have been infilled with organics. In the Plate 2 - Surficial Geology map, organics have been mapped only where they are thick and extensive. This, for the most part, occurs only in the northern third of the province where deposits of peat, usually Sphagnum, cover large areas of poorly drained terrain.

Because organics are considered more of a soil development than a surficial deposit, they will not be discussed in detail in this section.

3.3 HYDROGEOLOGY OF ALBERTA

Groundwater in Alberta is used extensively for domestic, municipal, industrial, and agricultural purposes. Any water well that is pumped at a continuous rate exceeding 23 $m^3 d^{-1}$ (3.5 imperial gallons per minute (igpm)) must be licenced by Alberta Environment. Figures provided by Alberta Environment indicate the following distribution in groundwater use in Alberta:

USE	NUMBER OF LICENCES	VOLUME OF GROUNDWATER USED
Industrial	770	50,163,500 m^3/year
Municipal	670	33,034,500 m^3/year
Agricultural	675	917,625 m^3/year
Miscellaneous	215	12,112,650 m^3/year
	2,330	96,228,275 m^3/year

The percentage breakdown of the licences, therefore, is: industrial (33%); municipal (29%); agriculture (28%); and, miscellaneous (9%). Gabert (1985) has examined groundwater use in Alberta and pointed out that for industry, 73% of the licences are for injection purposes related to secondary recovery of conventional crude oil or steam injection for exploitation of oil sands. Of the remainder, 19% are used for processing purposes and the rest are for miscellaneous uses.

Municipal use of groundwater is mainly for urban supplies (85%) and community supplies (14%). The remaining 1% is used for miscellaneous purposes such as recreation, parks, and campgrounds.

In addition, there are estimated to be in the order of 250,000 water wells used for domestic water supply. From 1975 to 1984, 60,492 new water wells were drilled in Alberta.

Annual demands for groundwater have been outlined for the five major river basins in Alberta (Gabert 1985) - the Peace, Athabasca, North Saskatchewan, Red Deer, and South Saskatchewan (Figure 44).

The main groundwater demand in the Peace River basin has been for industrial (mainly injection) use and secondarily for municipal purposes. Other demands have been small. With recent petroleum development in the area, groundwater demands were higher in 1984 than in previous years.

The Athabasca River basin groundwater demands have been similar to those of the Peace. Industrial use by the petroleum industry has been the primary water demand, followed by municipal use. Other uses (agriculture and domestic) are small. Demands have been highest for 1979 to 1983, with 1984 showing a decreased groundwater use.

In the North Saskatchewan River basin, the primary demand is for municipal use (urban and community water supplies). However, a strong demand exists for industrial use, particularly with the high activity in the Cold Lake/Lloydminster area. An increase in water supply demand has also been apparent for agricultural purposes, in particular, for feed lots.

In the Red Deer River basin, the main groundwater demands are for municipal and agricultural purposes. With increased enhanced recovery schemes and petro-chemical plants planned, industrial water demands have been increasing in recent years, most noticeably in 1984.

Industry demands the greatest amount of groundwater in the South Saskatchewan River basin with these demands situated mainly in the Medicine Hat area. Municipal demands are also significant. However, with surface water supplying irrigation supplies, agricultural demands are minimal.

Total Alberta licenced groundwater demand for the decade 1975 to 1984 was nearly 367,050,000 m^3. The North and South Saskatchewan River basins each had licenced groundwater demands exceeding 97,880,000 m^3 for this period. Requirements of 48,940,000 m^3 have been calculated for each of the Peace and Athabasca River basins and 61,175,000 m^3 for the Red Deer River basin.

Clearly, therefore, environmental phenomena that could impact on the groundwater resources of the province will be of concern to the public.

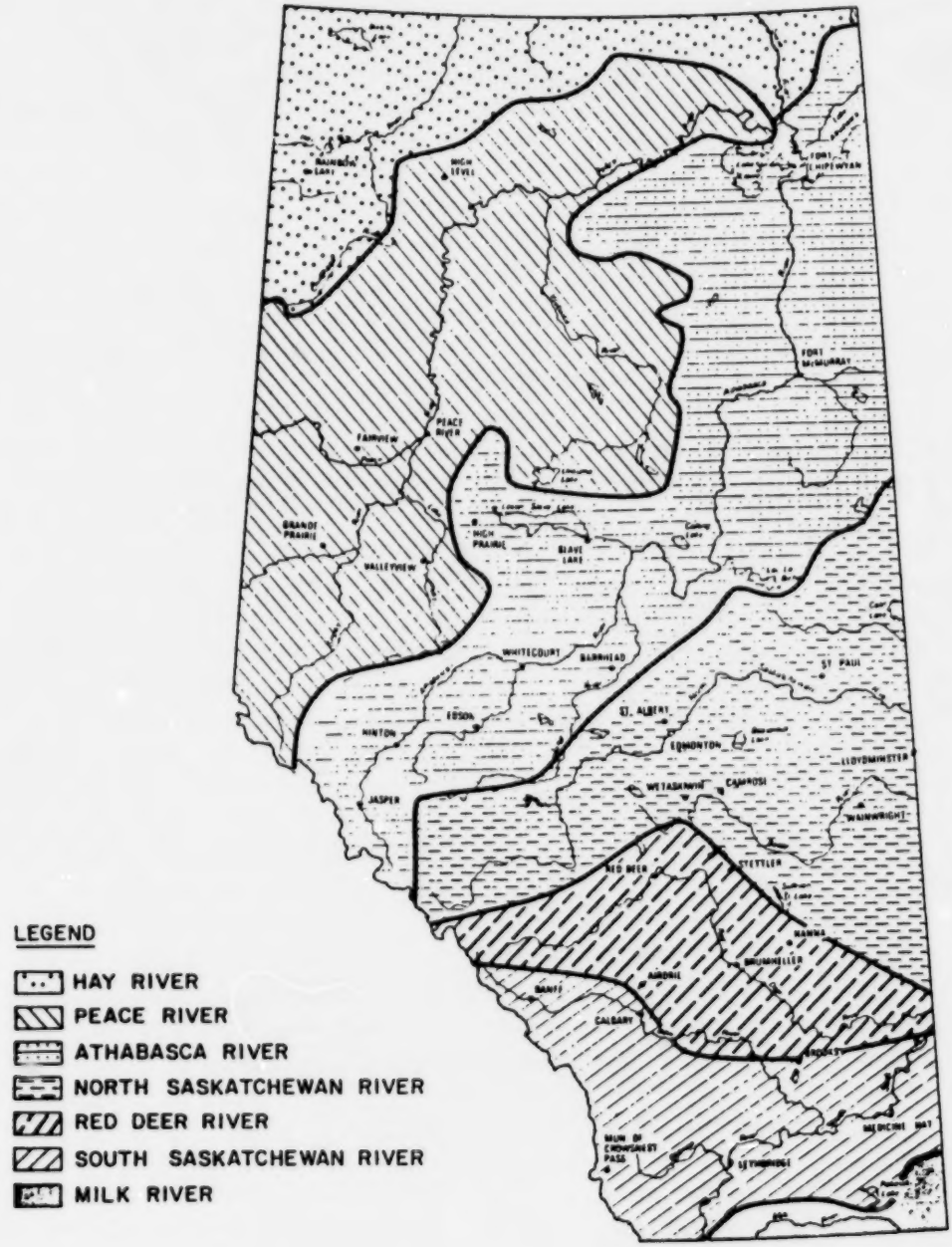

Figure 44. Major drainage basins of Alberta. Source: Gabert (1985)

Mapping of Alberta's hydrogeological resources has been undertaken by the Alberta Research Council. The maps (see Figure 45, Hydrogeological Map Coverage), published at a scale of 1:250,000, cover most of the province and consider groundwater chemistry, potential well yields, and an assessment of flow regimes.

On a regional basis, the order of magnitude of groundwater recharge is usually between 5% and 15% of precipitation.

The concept of the twenty-year safe yield is routinely used in Alberta to express the water yielding properties of aquifers. It implies that individual wells (spaced far enough apart so as not to influence each other) can be pumped for 20 years at that rate without drawing the water level in the well below the top of the aquifer. However, the 20-year safe yield calculation from actual pump tests is based on the static resources. If recharge is taken into account, the figure obtained for a well's yield is higher.

The frequency distribution of estimated 20-year safe yields in the upper 300 m (~1000 feet) of rocks was compiled (Figure 46) from hydrogeologic maps prepared by the Groundwater Divison of Alberta Research Council and from extrapolations based on geological conditions. The area of Alberta is 644,113 km^2 if the 16,789 km^2 lake surface is not taken into consideration. The results, in rounded numbers, are shown in Table 15.

Yields higher than 38 L/s (500 igpm) are found or expected at localities of only limited areal extent.

In the southern half of the province, sandstones are the major aquifers - notably, the Paskapoo Formation in west central Alberta, the Lower Belly River Formation in east central Alberta, and the Milk River Formation in the southernmost portion of the province. A major sand and gravel aquifer (buried channel) occurs east of Calgary.

In the the northern half of the province, sand and gravel aquifers occurring in buried valleys have the best potential for large groundwater supplies. Figure 42 in Section 3.2.3 shows the preglacial buried channels of Alberta.

Projections for groundwater use (Gabert 1985) suggest increasing demands in the northern half of the province for the petroleum industry and for municipal purposes as a result of the increased industry. In the southern half of the province, municipal use is expected to be strongest.

The chemistry of Alberta groundwater has been assessed on a regional scale and the results included in the hydrochemistry side maps of the hydrogeological maps prepared by the Groundwater Division, Alberta Research Council. The most common salts in groundwater in Alberta are sodium bicarbonate ($NaHCO_3$), calcium bicarbonate ($CaHCO_3$), common salt (sodium chloride, NaCl), and several kinds of sulphates (salts of the SO_4^{2-} ion).

In Alberta, results of a reconnaissance study on the distribution of nitrate in over 200 water table wells installed within a 750 km^2 area (Grisak 1975, cited by Hendry et al. 1984) yielded an average nitrate-nitrogen S concentration of 173 mg L^{-1} (range: 0-1711 mg L^{-1} NO_3-N). In subsequent studies in contiguous areas (Hendry 1981, cited by Hendry et al. 1984; 1982), nitrate concentrations up to 0.505 mg L^{-1} N in groundwater in tills were observed. These values are up to two orders of magnitude greater than the recommended standard of 10 mg L^{-1} for drinking water and so pose a severe health hazard. Previous studies on the nitrate contamination problem in southern Alberta (Grisak 1975,

Figure 45. Alberta hydrogeological reconnaissance map series.

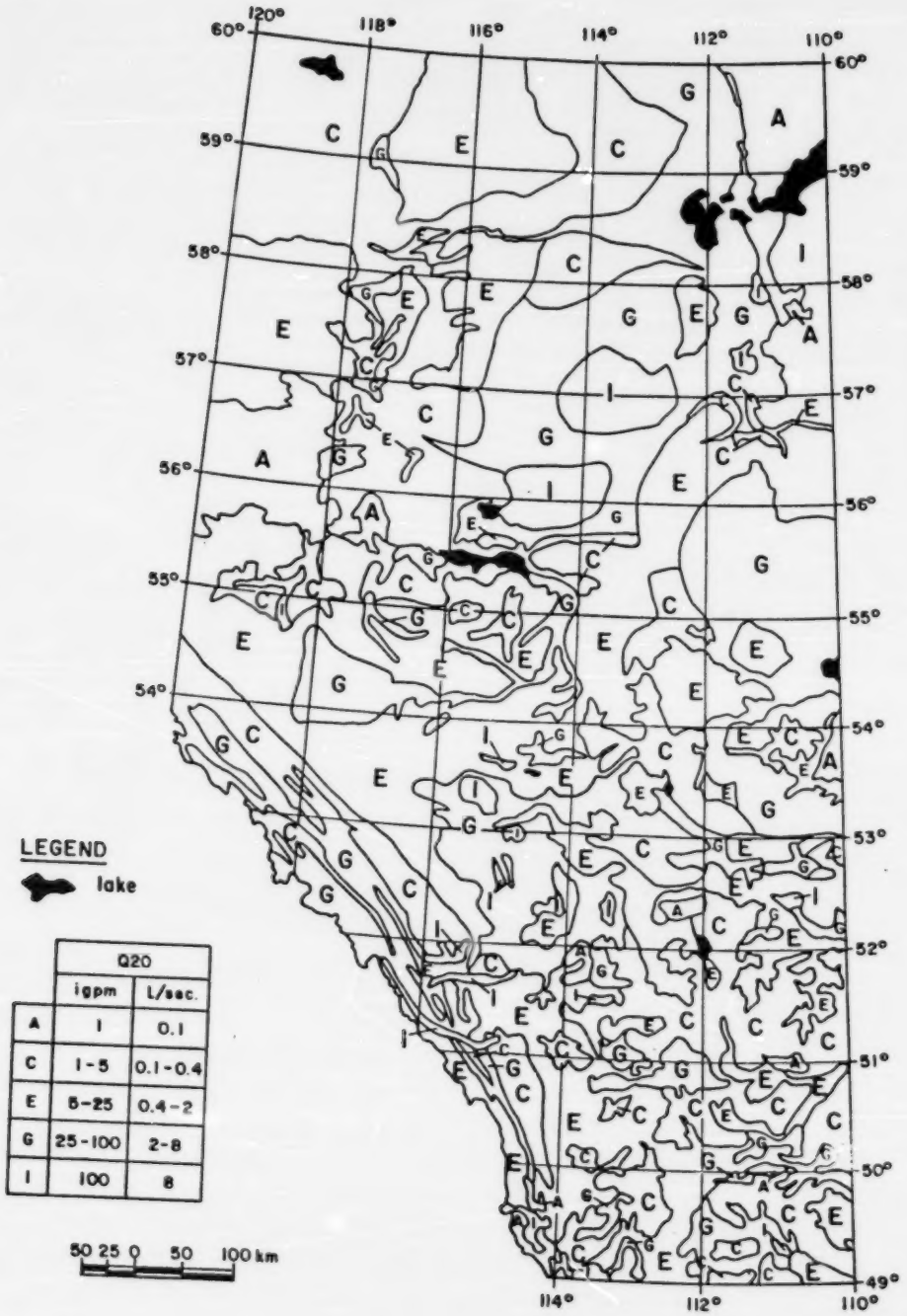

Figure 46. Areal distribution of 20-year safe yields (Q_{20}) from the uppermost 300 m in Alberta. Source: Gabert (1985)

Table 15. Twenty-year safe yield areal distribution summary for Alberta.

20-Year Safe Yield		Area	Percentage of
igpm*	L/s**	Thousand km²	Investigated Area
<1	<0.1	39	6
1-5	0.1-0.4	200	31
5-25	0.4-2	225	35
25-100	2-8	154	24
100-500	8-38	26	4
		644	100

* imperial gallons per minute
** litres per second

Source: Ozoray (1978)

cited by Hendry et al. 1984; Hendry et al. 1982, cited by Hendry et al. 1984) indicated that the nitrates originate from diffuse sources rather than point sources. After considering other nitrifying processes, Hendry et al. (1982, cited by Hendry et al. 1984) concluded that the oxidation of exchangeable NH_4^+, initially present in weathered till and still present in the nonweathered till, is the source of the high levels of nitrates. The presence of nitrifying bacteria and nitrifying potential in core samples from the weathered till indicates that indigenous microorganisms have the potential to oxidize exchangeable NH_4^+ to NO_3^- to depths of 30 metres. Hendry et al. (1984) also identified denitrifying processes that take place in both weathered and unweathered tills under anaerobic conditions. Three significant conclusions have been reached by this study:

1. Elevated nitrate concentrations can occur naturally as a result of oxidation of ammonium present in parent material.
2. These processes take place at a considerable depth below the soil horizon.
3. Denitrification potential was shown to exist below the present day water table.

A summary of the chemical characteristics of Alberta aquifers is shown in Table 16. When compared to the potability standards for Alberta and for Canadian Drinking Water (Table 14), it can be seen that many of the groundwaters in Alberta are technically unsuitable for human consumption due to excessive concentrations of specified ions.

The pH of groundwater in Alberta has not been extensively studied. However, numerous chemical data in the Groundwater Resource Information Services are available in unprocessed form that show the pH of groundwater in Alberta to be in the range of 6.0 - 8.5. The accuracy of specific pH values is somewhat suspect because the sampling methodology and sample handling is largely undefined. A study by the Alberta Research Council of selected groundwater in southern Alberta indicated a pH range from 6.1 to 8.45 (Balakrishna and Wallick 1982). It appears, therefore, that generally the pH values in the Groundwater Resource Information Services compare favourably with the pH values measured under rigorously controlled sampling procedures and handling. It must be kept in mind that few wells are completed in organic materials. As groundwater that is produced from organic deposits is aesthetically unattractive, domestic water supplies are seldom developed in organic materials. Therefore, few data are available on the pH or chemical constituents of groundwater from muskeg. Borneuf and Pretula (1980) observed in groundwater reconnaissance mapping in the Zama-Bistcho Lake area the presence of groundwaters with a pH value of less than 4.5. These waters exhibited variable total dissolved solid (TDS) values and were predominantly calcium or sodium nitrate type water. All these waters were related to the presence of muskeg. Ozoray (1974) reported similar TDS values in muskeg in the Waterways-Winifred Lake area. The muskeg waters in the recharge areas contain as little as 50 ppm dissolved solids. The muskegs and quasi-springs of the discharge areas contain up to 500 ppm.

Although little research has been done in Alberta on the geochemistry of groundwater in muskeg areas, it appears that pH levels may be depressed locally. Large portions of the northern part of the province are covered by organic deposits (see

Table 16. Field ranges and chemical types of groundwater in different geological formations of Alberta. (Source: Gabert et al. 1975, cited by Ozoray 1974)

Type of Rock	Characteristic Rock Unit	Part of Alberta	Characteristic Range of: Q20[1] igpm	Q20[1] L/sec	Type of Chemistry[2]	TDS ppm[3]
Present day river alluvium	Sand and gravel	In general	25-100	2-8	Ca/HCO_3	<500
	Sand and silt	In general	5-25	0.4-2	Ca/HCO_3	500
Preglacial channel gravel and sand	Main channels	In general	100-500	8-38	Ca/HCO_3 - Na/HCO_3	500-1000
	Tributary channels	In general	25-100	2-8	Na/HCO_3	1000-1500
Glaciolacustrine	Sands, beach sands	In general	5-25	0.4-2	Ca/HCO_3 - Na/HCO_3	800-1500
	Clay, silty clay	In general	>1-5	>0.1-0.4	Na/HCO_3 - Na/SO_4	1000-2000
Till	Ground moraine	In general	1-5	0.1-0.4	Ca/HCO_3 - Na/SO_4	800-1500
Coarse-grained	Part of Paskapoo F.	Central	100-500	8-38	Ca/HCO_3 - Na/HCO_3	500-1500
Coal	In Horseshoe Canyon F.	Central and southern	25-100	2-8	Na/HCO_3 - Na/SO_4	1000-2000
Moderately clean sandstone	Basal Belly River F.	Southern	5-25	0.4-2	Na/HCO_3	800-2000
	Paskapoo F.	Central	25-100	2-8	Ca/HCO_3 - Na/HCO_3	1000-1500
	Grand Rapids F.	Northern	5-25	0.4-2	Na/HCO_3 - Na/Cl	1500-3000
Sandstone with high clay content	Belly River F.	Southern	1-5	0.1-0.4	Na/SO_4	2000-3000
	Milk River F. (Marginal Part)	Southern	5-25	0.4-2	Na/Cl	10,000
	Milk River F.	Southern	5-100	0.4-8	Na/HCO_3	1000-2000
	Porcupine Hills F., St. Mary River F., Willow Creek F.	Southern	5-100	0.4-8	Ca/HCO_3 - Na/HCO_3	800-2000
	Clearwater F.	Northern	1-5	0.1-0.4	Na/HCO_3 - Na/Cl	2000-5000

continued...

Table 16 (Concluded).

Type of Rock	Characteristic Rock Unit	Part of Alberta	Characteristic Range of: Q20[1] igpm	Q20[1] L/sec	Type of Chemistry[2]	TDS ppm[3]
Shales	Horseshoe Canyon - fractured	Central	5-25	0.4-8	Na/HCO_3	1500-2500
	- non-fractured	Central	1-5	0.1-0.4	Na/HCO_3	1500-2500
	Bearpaw F., Pakowk F.	Southern	<1	<0.1	Na/SO_4	2000-3000
	LaBiche F., Joli Fou F.	Northern	<1	<0.1	Na/SO_4 - Na/Cl	2000-3000
Limestone and dolomite	Waterways F.	Northern	25-100	2-8	Na/Cl	2000-10,000
	Paleozoic	Western	25-100 occ. over 500	2-8 occ. >38	Ca/HCO_3	500-1000
Evaporite	Devonian	Northern	<1-5	<0.1-0.4	Na/SO_4 - Na/Cl	10,000-100,000
Crystalline (such as granite), igneous, metamorphic, and metasedimentary rocks	Proterozoic Archean	Northern	<1	<0.1	Mixed	50-500

1 Twenty-year safe yield, imperial gallons per minute, one litre per second.

2 Chemical type is given by the main cation on the left side, separated by / from the main anion on the right side:
Ca = calcium and magnesium together (Ca^{2+} and Mg^{2+})
Na = sodium and potassium together (Na^{+} and K^{+})
HCO_3 = carbonate and bicarbonate together (CO_3^{2-} and HCO_3^{-})
SO_4 = sulfate (SO_4^{2-})
Cl = chloride (Cl^{-})

3 Total dissolved salts, parts per million

surficial geology map, Plate 2); the near surface pH of groundwater in a large percentage of these areas could be acidic. Work by Schwartz (1980), however, indicated that muskeg in Alberta may not be as acidic as has been reported elsewhere. Measurements of pH in groundwater from muskeg deposits in the Muskeg River basin of northeastern Alberta show a pH range generally exceeding 6.5. Of 144 samples of groundwater analysed during the Schwartz study, only three samples had a pH below 6.0. The lowest value, however, was 1.98.

There are marked differences in groundwater conditions of different parts of Alberta resulting from differences in geology (Green 1972), topography, climate, vegetation, and soils. Figure 47 shows the groundwater regions of Alberta based on these environmental factors.

More detailed hydrogeological assessments have been undertaken in Alberta usually as part of groundwater supply studies. The results of these water supply studies are usually incorporated into reports prepared by hydrogeological consultants, and submitted to Alberta Environment as part of the regulatory process. They become part of the public domain through the Groundwater Resources Information Services provided by Alberta Environment. Likewise, records of water wells drilled in Alberta and chemical analyses have been maintained in the Groundwater Resources Information Services since the 1930's.

The regional (1:250,000) scale maps produced by the Alberta Research Council show the hydrochemistry of Alberta's groundwater to be complex and spatially variable. Studies conducted on groundwater in Alberta (Monenco Consultants Limited 1986) indicate that temporal changes in groundwater chemistry are commonplace. Little information is available on the distribution of heavy metals in Alberta groundwaters except from unpublished environmental assessments undertaken by industry or government agencies.

The path followed by groundwater once it has entered the subsurface is determined by geology, topography, and gravity. Toth (1963) has suggested that in most hydrogeologic settings, one can differentiate between local, intermediate, and regional systems of groundwater flow. Where local relief is negligible, only regional systems develop. Where there is pronounced local relief, only local systems develop. Figure 47 makes it clear that even in basins underlain by homogeneous isotropic geologic materials, topography can create complex systems of groundwater flow. The only immutable law states that highlands are groundwater recharge areas and lowlands are groundwater discharge areas. Spatially, discharge areas constitute an average of only 5.3% of the surface area of a watershed.

At any specific location, therefore, the degree of penetration of atmospheric deposition into the subsurface may depend upon whether the location is in a recharge or discharge area, or if the recharge took place in an area of heavy atmospheric loading.

In the Alberta setting, it is possible to recognize the three types of flow regimes identified by Toth (1963). Regional hydrogeological maps produced by the Alberta Research Council provide numerous examples of regional and intermediate flow regimes. Local flow regimes, because of their smaller scale, have not been documented by the regional mapping effort as frequently as the large groundwater flow systems.

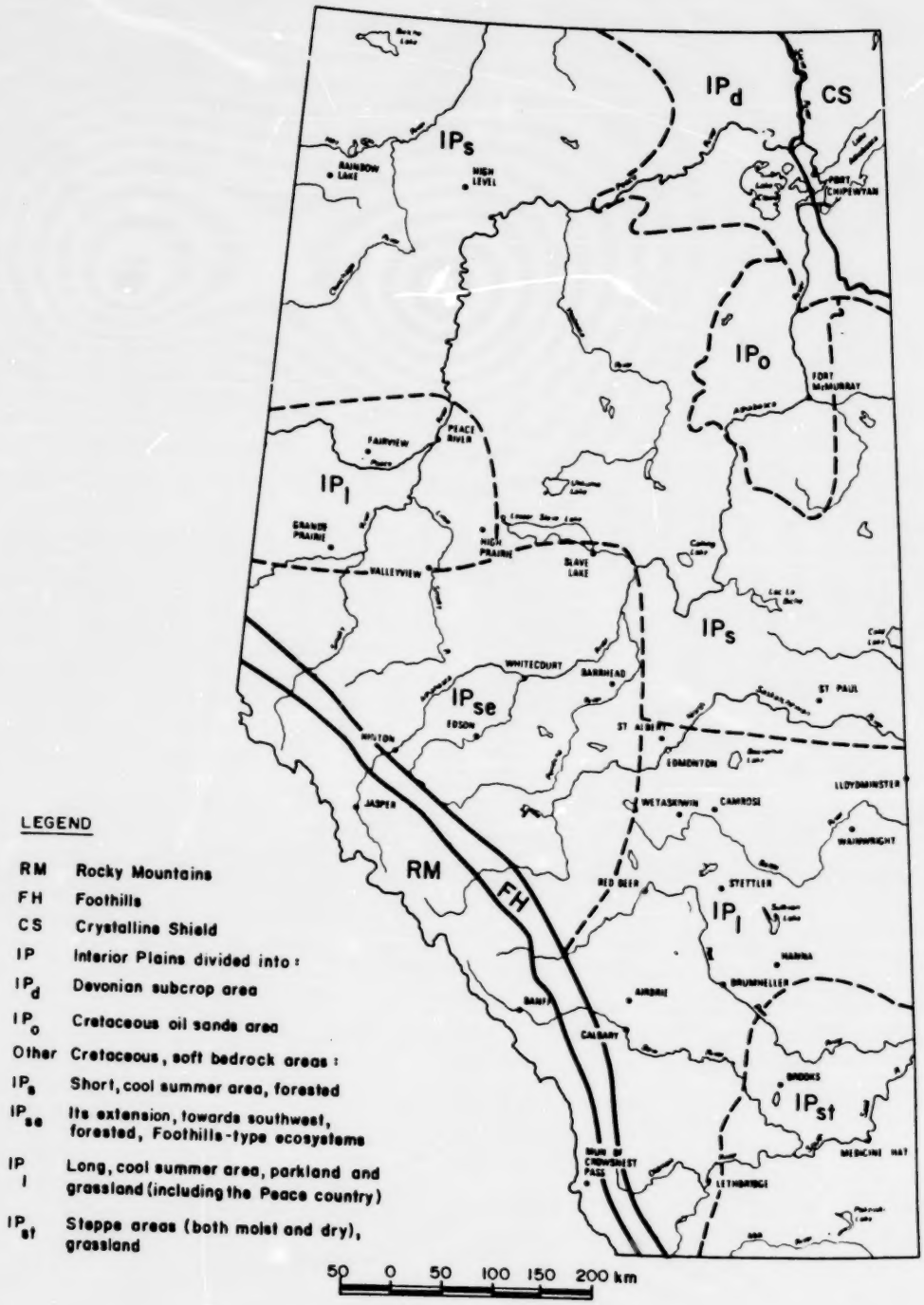

Figure 47. Groundwater regions of Alberta. Source: Ozoray (1978)

4. CONCLUSIONS AND IMPLICATIONS

Based on our understanding of the science of hydrogeology and our understanding of acidic deposition, there is a reasonable scientific basis for concern about the impact of "acid rain" on our groundwater resources. There is strong scientific evidence, particularly from Sweden, that relates acidic deposition to changes in groundwater chemistry, although the evidence is not conclusive in a regional context. In Canada, there is no conclusive evidence of changes in groundwater chemistry due to acidic deposition. While it is recognized that acidic groundwater conditions do exist locally in parts of Canada, these acidic conditions have not been related to acidic deposition. It has been concluded by the studies on groundwater conducted in Ontario that, given sufficient atmospheric loading over a long enough time period, changes in groundwater chemistry would occur.

The groundwater resources in the province of Alberta are utilized extensively for domestic, agricultural, municipal, and industrial purposes. Changes in groundwater chemistry in Alberta, therefore, could have a dramatic effect on the well-being of persons relying on groundwater for their water supply.

The groundwaters in Alberta are characterized by relatively high pH values (6.5-8.0) and high acid neutralization capacity. As well, on a regional basis, bedrock and surficial deposits tend to have a high acid neutralization capacity due to high carbonate contents and are less susceptible to acidification than other geological settings found in Sweden and the eastern part of North America. Although the availability of groundwater chemistry data in the northern part of Alberta is limited, evidence that is available suggests that even in the muskeg areas, groundwater chemistry is characterized by pH values in the 6.5-8.0 range.

Much of Alberta is covered with relatively thick deposits of glacial till that have a high acid neutralization capacity. It is doubtful if acidification of groundwater in these deposits would occur in the short term given the present level of atmospheric loading. It may, however, be possible to see the residues or by-products of the acid neutralization process even though the pH of the groundwater has not been noticeably altered.

Based on our present understanding of hydrogeology and acidic deposition in Alberta, it is concluded that acidification of groundwater is not a regional problem. At the present time, there is no evidence that acidic deposition has had any negative impact on groundwater in Alberta, although Krouse et al. (1984) have found isotopic evidence in the West Whitecourt area which suggests that the products of neutralization have reached the water table.

Studies in Sweden show that under selected acid loading rates, the acid neutralization capacity of a geological medium can be depleted over a period of 10 to 60 years. No estimates are available of rates of depletion of acid neutralization capacity for geological materials in Alberta.

It is likely that over a sufficiently long period of time, the chemistry of groundwater in Alberta will be modified by acidic deposition. There are, however, no data available to support this theoretical conclusion. It is not known what acid loading scenarios might result in these local impacts. No groundwater assessments have been undertaken in Alberta to determine background levels of acidity or acidification

potential. Acidification of groundwater as reflected by changes in pH may constitute a corrosion problem, but in itself, this is not a health hazard.

Should groundwater become acidified from acidic deposition or other causes, increased mobility of certain metals in the subsurface can be anticipated. The presence of these metals in domestic or municipal water supplies may constitute a health hazard under certain circumstances. The potential risk to human health from corrosion of water distribution systems by acid waters has been recognized as well.

Sufficient information is available to conclude that if groundwater in Alberta was acidified to a pH of 3.5 - 4.0, there would be reason for concern regarding human health. The mobilization of heavy and trace metals in acidic groundwater is a health concern, but not necessarily a problem. The degree to which groundwater has been impacted by acidic deposition is not clear. Acidic groundwater which contains metal concentrations at or near the accepted limits has been identified in Europe, the US, and Canada. Increases in the mobility of metals in groundwater will occur with decreases in alkalinity and pH. The mechanisms of metal mobilization in the saturated and unsaturated zone are complex and cannot be adequately explained with simple leaching tests.

Information currently available in the literature on the chemistry of heavy metals in natural waters and soils makes it clear that metal solubility in natural aqueous systems can be influenced by:

1. organic materials;
2. clay minerals;
3. metal hydroxides;
4. pH; and
5. divalent ions

Metals that have been cited in the literature as being of concern from a hydrogeological point of view are: lead; manganese; mercury; chromium; aluminum; iron; copper; nickel; zinc; selenium; and cadmium.

Other constituents include: SO_4^{2-} (sulphate); NO_3^- (nitrate); Ca (calcium); SiO_2 (silica); Mg (magnesium); K (potassium); and Na (sodium).

The preliminary conclusions that we have reached regarding siting of studies on acidic deposition effects on groundwater are generally consistent with the conclusions reached by Parkinson and Legge (1985). We believe that the past and present impact of acidic deposition on groundwater in Alberta is likely to be very low to non-detectable due to the relatively low loading rates and the generally high buffering capacities of near-surface geological materials.

We have concluded that two general criteria should be met by the research site:

1. the site should be located in an area of relatively heavy acidic deposition; and
2. the hydrogeological regime in the research area should be such that the impact of acidic deposition can be documented within the time frame of the project.

The hydrogeological regimes that are likely to show a documentable response to acidic deposition should display:

1. low buffering capacity;
2. rapid recharge;
3. shallow, easily traceable flow regime; and
4. high permeability, that when coupled with a short flow path, would result in a short residence time for groundwater in the formation.

Geological settings that are likely to reflect the above-mentioned hydrogeological characteristics would be located where aeolian or glacial outwash deposits overlie dense, low permeability glacial till or bedrock. It would be desirable to locate the research site in a local flow regime within a regional recharge area, thus avoiding the potential confusion that could result from siting in a location where both local and regional discharge conditions exist.

It is felt that the past and present impact of acidic deposition on groundwater is extremely low in hydrogeological settings where surficial deposits have a high buffering capacity. If the major direction of groundwater movement is vertically downward, it will be extremely difficult if not impossible to accurately document the impact of the relatively light acidic deposition on the hydrogeological regime. Temporal variations in groundwater chemistry in Alberta, particularly in shallow water table aquifers, may mask geochemical changes in groundwater caused by acidic deposition.

It is apparent from existing data that sulphates (SO_4^{2-}) are a common constituent of prairie groundwaters with concentrations ranging from 0 to several hundreds of mg L^{-1}. Temporal or seasonal variations in sulphate levels, although not well documented, are known to range up to several tens of mg L^{-1}. In such a geochemical setting, the contribution of small amounts of atmospheric deposition may not be easily detected.

Likewise, Hendry (1984) has identified naturally occurring nitrate concentrations over large areas of southern Alberta. Until recently, nitrates in groundwater in Alberta were generally assumed to originate from agricultural or domestic sewage, or from agricultural fertilizers. It is apparent from Hendry's work that the source nitrate in groundwater needs further consideration, and any study of the impact of atmospheric deposition must have a firm scientific handle on both the natural and anthropogenic processes that contribute nitrates to the groundwater regime.

The impact of acidic deposition on groundwater is likely to be very subtle and it is desirable that extraneous factors that potentially affect the groundwater chemistry on the research site should be stabilized for the duration of the project. Extraneous factors that could have an impact on groundwater chemistry include, for example, the application of fertilizer, changes in cropping patterns, changes in vegetation cover, and disturbance of the soil horizon. As most of these extraneous factors are man-induced, it is desirable that the projects are located in areas where anthropogenic modification of the site will be minimal during the research period.

The ability of science to evaluate and predict the mechanisms affecting hydrology is more advanced than the science to evaluate geochemical and biochemical aspects. In the assessment of the impact of acidic deposition on the terrestrial environment, the hydrologic component should be relatively straightforward in that it will involve the application of existing science and does not necessarily require the development of new techniques or methodology.

The impact of acidic deposition on groundwater is a function of a number of physical properties of the aquifer as well as loading. The movement and flowpath of the groundwater has a profound effect on groundwater chemistry. As well, changes in hydraulic conductivity of geological materials can be induced by acidic deposition and, therefore, changes in basin hydrology may occur.

5. DEFINITION OF DATA DEFICIENCIES AND RESEARCH NEEDS

Based on the review of existing literature and a regional review of the hydrogeology of Alberta, it has been hypothesized that there is a limited risk of widespread impacts on groundwater chemistry. Locally, however, certain aquifers may be more sensitive to acidic deposition than others. Unfortunately, there are no data presently available in Alberta to support or refute this hypothesis.

It is felt, therefore, that in order to meet the objectives of the ADRP, the hypothesis must be tested. In order to test this hypothesis, it is recommended that a study be undertaken to: (a) document the response of the most sensitive aquifers in Alberta to acid loading; and, (b) document the response of moderate- or low-sensitivity aquifers in Alberta to acid loading. The objective of such a study should be to observe and quantify the nature and magnitude of changes in groundwater chemistry due to acidic deposition.

There is very little information available regarding temporal or seasonal fluctuations in groundwater chemistry in Alberta, nor is there a clear understanding of baseline groundwater chemistry in the province, particularly with regard to metals. Any project designed to evaluate the impact of acidic deposition on groundwater must be able to differentiate between temporal or seasonal changes in groundwater chemistry and those changes induced by acidic deposition. Indeed, it may be that in certain hydrogeological settings on the prairies, temporal variations in groundwater chemistry may totally mask the impacts of acidic deposition. In such cases, the use of stable isotopes may be a useful tool in assessment.

The literature indicates that in Europe and eastern North America, depressed pH values are associated with bogs and muskeg. As such, these areas are considered sensitive to further acidification from atmospheric deposition. The limited information available on the groundwater chemistry in muskegs in Alberta does not support the conclusion that pH values are universally depressed. The data in fact show that pH values in muskeg are for the most part very similar to pH values seen in groundwater derived from bedrock or surficial deposits (i.e., pH 6.5-8.0). Because such a large area of Alberta is covered with muskeg and organics, it is critical to the assessment of sensitivity that the pH and geochemistry of these areas be understood. It is recommended therefore, that a study be undertaken to: (a) characterize the chemistry of groundwater in muskeg areas of the province; and, (b) determine what geochemical processes influence the quality of groundwater in muskeg areas.

Although hydrogeological maps have been produced for the entire province, the scale of these maps limits their use in evaluating hydrogeological settings that are local in scale. As well, much of the groundwater data available from the Groundwater Resources Information Services are of limited use because of substandard quality and data density.

There are, however, a number of areas and/or basins in the province that have been studied in some detail. In locating the ADRP research sites, some consideration should be given to those sites where control is available by virtue of previous studies conducted in the area.

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